

1942

# The photochemistry of the formation of sulfuryl chloride

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THE PHOTOCHEMISTRY OF  
THE FORMATION OF SULFURYL CHLORIDE

by

Martin Christopher Londergan

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject: Physical Chemistry

Approved:

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1942

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## I. INTRODUCTION

The fundamental laws of photochemistry date back to Grotthuss (1) in 1817. As formulated by him and later by Draper (2) in 1839, the law which bears their names states that only the light which is absorbed can produce a chemical change.

The development of photochemistry as an exact science proceeded very slowly, and it was not until the application of the quantum theory to chemical reactions by Einstein (3) in 1912 that the results could be placed on a quantitative basis. Later developments have indicated that radiations are absorbed in a material body in units or quanta and through this absorption the body becomes activated and in some cases capable of reacting. If a reaction takes place, the primary process should be one in which one atom or molecule should react for each quantum of light absorbed. The over-all reaction differs from the primary process in that secondary reactions, wall effects, and deactivations of many types show the result that the numbers of molecules reacting for each quantum of radiation absorbed (quantum efficiency) may vary from a very small fraction to  $10^6$ . It is generally accepted that the primary process in a photochemical reaction depends upon the activation of an atom or molecule by the absorption of a quantum of light. The over-all reaction would result from any secondary reactions added to this primary process.

A survey was made in the field of photochemistry for a

reaction which might be used in the separation of isotopes; the reaction of sulfur dioxide and chlorine offered the best possibilities.

The theory to be tested in this method of isotopic separation depends upon the selective absorption of light by one type of an isotopic atom or molecule over another in an isotopic mixture. Taking chlorine as an example, there are about 3.35 chlorine atoms with an atomic weight of 35 to every chlorine atom with an atomic weight of 37.\* This gives a mixture of three types of molecules  $\text{Cl}_{35}\text{Cl}_{35}$ ,  $\text{Cl}_{35}\text{Cl}_{37}$ , and  $\text{Cl}_{37}\text{Cl}_{37}$  in the ratio 11.3 to 6.7 to 1. Using one tube of chlorine gas as a filter to remove all the light which could be absorbed by the  $\text{Cl}_{35}\text{Cl}_{35}$  molecule, there should be a larger fraction of the light passing through the filter which could be absorbed by the  $\text{Cl}_{37}\text{Cl}_{37}$  molecule. This light, which had already passed through the first tube of chlorine, would then enter a second tube that also contains chlorine gas. This second tube would contain another substance besides the chlorine which would react with the activated chlorine molecules. The light entering the second tube could activate only the  $\text{Cl}_{37}\text{Cl}_{37}$  molecule as all had been absorbed which would activate the  $\text{Cl}_{35}\text{Cl}_{35}$ . The resulting product after activation should contain a much larger percentage of  $\text{Cl}_{37}$  than one formed using the usual chlorine gas. If sulfur dioxide were the second molecule present, the sulfuryl chloride which was formed should be enriched in  $\text{Cl}_{37}$ .

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\*These values are given by Elliot; Proc. Roy. Soc. (London), A123, 629-44. 1929.



In the choice of a reaction of this type several factors had to be considered. There must of necessity be isotopes present in the absorbing molecule in such a ratio that the light would be selectively absorbed by one type of the isotopic component. There should be no chain reactions and very few, if any, side reactions. The quantum efficiency, which is the ratio of the number of molecules of the product formed to the number of quanta of light absorbed, should be one.

The reaction of sulfur dioxide and chlorine upon the activation by monochromatic light seemed to fulfill these conditions. It was necessary though that a thorough study of this reaction be made under various experimental conditions before an attempt could be made to separate the isotopes of chlorine by this method. It is on this phase of the problem that this investigation has been performed.

## II. HISTORICAL

Regnault (4) in 1811 has given the first recorded observation that sulfur dioxide and chlorine combine under the influence of light. He observed that if the two gases were mixed and exposed to the strong rays of the summer sun, a liquid condensed on the walls of the vessel. Likewise, he noticed that very little or none of the liquid formed when the mixture was exposed to the rays of the winter sun, <sup>step</sup> indicating that the reaction was probably due to the shorter radiations which would be much weaker during the winter months.

Trautz (5) in 1908 measured the vapor pressure of sulfuryl chloride and determined the decomposition of the gas in the region of  $100^{\circ}$  to  $200^{\circ}$  C. From these data he calculated the constants in the Nernst specific heat equation, and from these calculations he has given a curve to show the decomposition of the compound from  $-80^{\circ}$  to  $300^{\circ}$  C. It was necessary to use a catalyst for the decomposition at the temperature which he worked. Activated charcoal gave the best results in this decomposition.

In a later paper Trautz (6) showed that the photochemical formation of sulfuryl chloride gave a stationary concentration which was higher than the thermal equilibrium at the same temperature.

Le Blanc, Andrich and Kangro (7) made a study of the photochemical system of a mixture of sulfur dioxide, chlorine and

sulfuryl chloride in order to establish the effect of light of different wave lengths upon the reaction mixture. The absorption spectra of chlorine, sulfur dioxide and sulfuryl chloride show strong maxima in different regions of the spectrum. That of chlorine is about 3400 A, sulfur dioxide is about 3000 A, and sulfuryl chloride shows a maximum of absorption below 2500 A. This afforded a method of studying the effect of light upon the mixture which would activate only one of each of the three types of molecules in the mixture. They found that light below 2500 A, which was absorbed by the sulfuryl chloride, caused decomposition into sulfur dioxide and chlorine as well as possibly some other products in small amounts. When the mixture was illuminated with light in the region of 3000 A, which was absorbed by the sulfur dioxide, they found a slight decomposition of the sulfur dioxide but no other reaction. If a mixture of sulfur dioxide and chlorine was illuminated with light above 3000 A, this light being absorbed by the chlorine, the reaction proceeded toward the formation of sulfuryl chloride. Air was present as a cushion to keep the chlorine and sulfur dioxide from coming in contact with the mercury in the manometer; water vapor and more air were added in some reactions, but these had very little effect on the formation of sulfuryl chloride. Thus, they established the fact that it is the light which is absorbed by the chlorine in a mixture of sulfur dioxide and chlorine which causes the photo-chemical formation of sulfuryl chloride to take place.

Tramm (8) indicated that pure and thoroughly dried chlorine

and sulfur dioxide tend to react much more slowly than if moisture is present. Later work by Schultze (9) has thrown doubt upon this work of Tramm because it was shown in an extensive set of experiments that water vapor had no noticeable effect on the photochemical formation of phosgene from carbon monoxide and chlorine. This reaction had also been claimed by Tramm to be strongly retarded if the gases were thoroughly dried.

Bonhoeffer (10) has given an approximate quantum efficiency for the reaction of sulfur dioxide and chlorine as about one thousandth of that of phosgene. This would be about one or two as his values for phosgene were of the order of  $2 \times 10^3$ .

A summarized review shows that the reaction of sulfur dioxide and chlorine proceeds in the formation of sulfuryl chloride when the mixture is illuminated with light that is absorbed by the chlorine. The reaction has very few or no side reactions and has a quantum efficiency which is of the order of unity. The reaction can be carried out at ordinary temperatures and pressures and, as there is a change in the number of molecules during the process, the extent of the reaction can be followed by noting the change in pressure. One of the objectional features in the previous work on this reaction has been the methods of measuring pressure changes. Corrections had to be made for the gases which were absorbed in the manometer liquid during the extent of the reaction. Le Blanc, Andrich and Kangro (7) tried to overcome this by having a cushion of air between the gases and the manometer liquid, but this method allowed air to diffuse slowly through the gaseous mixture.

### III. EXPERIMENTAL INVESTIGATION

#### A. Apparatus

##### 1. Light source

A General Electric capillary quartz mercury arc (type H6) which operates at 80 atmospheres internal pressure was used throughout the investigation. This arc gave an intense beam in the blue region of the spectrum. The capillary was made of quartz about 2.0 mm. inside diameter and 2.5 cm. in length, with tungsten electrodes sealed in each end. The arc operated in a horizontal position, surrounded by a pyrex water jacket through which water flowed at the rate of about six quarts a minute. It operated on 1200 volts from a General Electric transformer and the total power input of the arc was about 1000 watts.

The beam was rendered approximately parallel by a cylindrical glass lens with a focal length of 24 mm. It was then passed through two iris diaphragms to remove most of the light which was not parallel.

In the experiments in which monochromatic light was used, a Corning filter (No. 7) was placed between the two iris diaphragms to isolate the 4358 A line of mercury. This filter allowed very little light other than that of the 4358 A line to pass through, but the intensity of this light was decreased to about fourteen

per cent of the original value. For this reason, monochromatic light was used only in those runs in which the quantum yield was determined because the speed of the reaction was greatly reduced with the decreased intensity of the beam.

This type of arc proved very satisfactory as an intense source of radiation. There was no trouble experienced in obtaining continuous operation, and after the first few hours there was very little change in the intensity of the beam throughout the lifetime of the arc. There was though an appreciable variation in the intensity from hour to hour due to the fluctuations in the line voltage.

## 2. Reaction chamber and method of stirring

The reaction chamber was a pyrex tube 4.8 cm. in diameter and 108.4 cm. in length. This had a capacity of 3340 cc. The faces were of smooth pyrex which were fused on the end of the tube, using a modification of the method of Fairchild (11). The chamber was painted black to exclude all light other than that of the beam from the mercury arc.

It was found to be necessary to circulate the gases in the reaction chamber, especially when a narrow beam of light was used, in order to prevent any filtering effect resulting from a change in concentration which would not be the same throughout the system. Because of the corrosive nature of the gases used, it was necessary to use a pump of such construction that no metal would be in contact with the gases at any time. A pump

similar to that described by Livingston (12) was built and is shown in 2 , Fig. 1. The gas was circulated by a piston moving in the fields of two solenoids. The piston was a piece of soft iron about six inches in length and a half inch in diameter, sealed inside a pyrex tube. This piston moved inside a cylinder of pyrex tubing 22 mm. in diameter. The inside of this cylinder was ground smooth to prevent the piston from sticking. As the valves were made of small glass bulbs, there was nothing present which could affect the purity of the gases. The valves were made in the shape of an inverted pear to prevent sticking and were ground into the valve seats so they would hold a pressure of about six inches of mercury.

The solenoids were wound with No. 22 magnet wire, about 2000 turns to each coil. These two coils, each three inches in length, were wound on a pyrex tube with a space of about an inch between them to facilitate cooling. With these solenoids thirty volts (DC) and a current of 2.5 amperes were used to move the piston.

Various methods were tried for alternately passing the current through each of the two solenoids. That which was found to be the most successful was a small motor which was geared down to operate a cam at ten revolutions per minute. This cam then tilted a mercury switch which had contacts at both ends and in the middle. Thus, contact would be made first with one coil and then the other. In this way, with the cam turning slowly, the piston stopped in each coil before the circuit was broken,

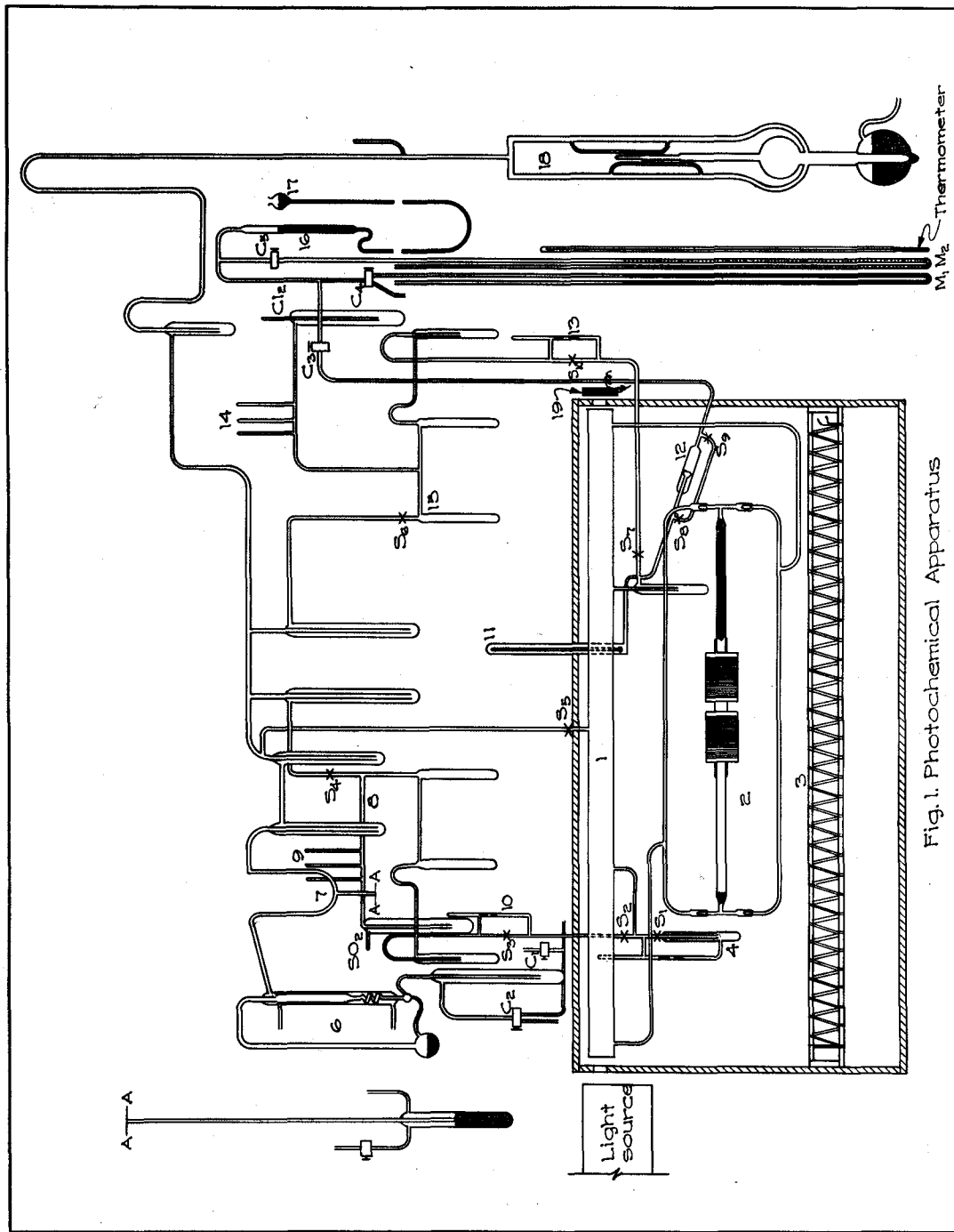


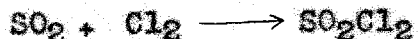
Fig. 1. Photochemical Apparatus



giving little chance for the piston to move out of the field and hit the end of the tube. Glass springs and a small amount of glass wool were placed in the ends of the cylinder to prevent the piston from going through the end of the tube in case it happened to leave the field of the solenoid before contact had been made with the other coil.

### 3. Manometer and pressure measurements

The extent of the reaction was determined by the measurement of the pressure change in the system:



One volume of sulfur dioxide reacted with one volume of chlorine to give one volume of sulfuryl chloride. Thus, there was a decrease in the volume of the system as the reaction proceeded. The total decrease was equal to the volume of sulfuryl chloride formed, assuming the relationship:

$$PV = nRT$$

would hold over this small range of pressure change.

The usual methods of pressure measurement could not be applied satisfactorily because of the corrosive nature of the gases. It was necessary that the pressure measurements range from less than 1 mm. up to atmospheric pressure. A combination manometer and click gage described by Smith and Taylor (13) was found to give the most consistent results (12, Fig. 1). In this method the pressure was read as the difference in the heights of a liquid in the legs of a manometer (M1, Fig. 1) but a thin

glass diaphragm separated the manometer from the system whose pressure was being determined. This glass diaphragm was thin enough so that a small excess pressure on either side caused an audible click as the diaphragm snapped in moving towards the lower pressure. Thus, as the pressure which was being measured would decrease, a click would be heard when the pressure became a definite amount less than that of the manometer; as the pressure of the manometer was decreased, a click was audible when it became less than the pressure in the system. The pressure in the system could be determined at any time by raising or lowering the leveling bulb, (17, Fig. 1); increasing or decreasing the pressure above the manometer caused the gage to click.

The gage was built by blowing a thin bulb on the end of a pyrex tube 6 mm. in diameter; while still hot the end of the bulb was flattened on a piece of flat carbon. Many attempts were made to obtain one with the approximate characteristics that were desired. They had to be thin enough to click but still strong enough to withstand a change of at least half an atmosphere of pressure on either side. Ten of these were made and five were broken in attempts to calibrate them. Three were broken after they had been calibrated and assembled into the apparatus in attempting to pump the system down or upon admitting the gases to the evacuated apparatus.

A method was finally devised in which a vacuum stopcock (C3, Fig. 1) was used to connect the manometer and leveling bulb with the click gage. A tube was sealed to each side of

the click gage to act as a by-pass while the system was being evacuated against the stopcock (C3). After the system was evacuated this tube was sealed off (S8 and S9, Fig. 1). The manometer system was then pumped down to about 2 cm. Hg pressure and the stopcock (C3) could be opened slowly, allowing the manometer (M1) to be connected directly to one side of the click gage.

The gage was mounted on the apparatus with the inside of the bulb towards the system which was evacuated. This was necessary in order that the natural position of the diaphragm with the pressure the same on both sides would be such that it would take an added pressure on the manometer side to cause the gage to click. The excess pressure which was necessary on the manometer side was 24.44 cm. Hg\* and this did not vary more than .03 cm. Hg over the entire pressure range. This was calibrated at 70° C. at which temperature the experiments were run. At room temperature the click was much louder and the same pressure (24.44 cm. Hg) was needed in order to cause the diaphragm to click.

In the first experiments the pressure differences were read by means of a mercury manometer (M1, Fig. 1). An open end manometer was used to prevent any error due to small amounts of gas above the mercury in a closed manometer. Temperature corrections were made if the temperature varied more than a degree. With the use of an open end manometer it was necessary to read

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\*All pressures corrected to cm. Hg at 25°.

the barometer and make corrections for the brass scale.

In the later experiments an auxiliary manometer containing  $\alpha$ -bromonaphthalene ( $d_{20}^{20}$  1.426) was used to read the pressure differences during a run. This manometer could be used only when the pressure inside the system was within the range of  $\pm 8$  cm. Hg of atmospheric pressure minus that necessary to click the gage. This necessitated a total starting pressure of about 52 cm. Hg inside the reaction chamber, and as the total pressure change during the extent of the reaction was of the order of 4.0 cm. Hg these differences could easily be read on the  $\alpha$ -bromonaphthalene manometer. Using the lighter liquid, the total change during the reactions was about 35 cm., increasing the accuracy considerably. The maximum error using the mercury manometer was  $\pm .05$  cm. Hg while the maximum error with the  $\alpha$ -bromonaphthalene manometer was  $\pm .03$  cm. Hg.

The mercury manometer had to be used in the measurement of the pressures of the gases as they were admitted because of the limited range of the lighter liquid. The actual manipulation and reading of the pressure will be given in part C under this heading.

The system was pumped down at 5, Fig. 1 with a hy-vac pump and then the mercury diffusion pump (6) was turned on to complete the evacuation. This evacuation always took over twenty-four hours with the reaction chamber heated to nearly a hundred degrees and the apparatus outside the constant temperature bath was heated with the smoky flame from a torch in order to drive

out the last traces of vapor. These low pressures were read on a multiple-stage McLeod gage which was calibrated to read pressures varying from 1 mm. Hg to  $10^{-6}$  mm. Hg. The system was always pumped down below  $10^{-5}$  mm. Hg before the gases were admitted.

The only stopcocks in the system (C1 and C2) were vacuum type and aided in pumping the apparatus down. They were sealed off from the rest of the apparatus before the gases were admitted so there could be no contact between the gases and the stopcock grease. The mercury cut-off 7 made it possible to close the system to the vacuum pumps by a column of mercury. In place of stopcocks small glass tips 4, 9, 13 and 14 were used. These tips were sealed inside a tube and could be broken by lifting a small piece of glass-enclosed soft iron with an electromagnet and then allowing it to drop on the tip. This method required much more time than the use of stopcocks but there was no contact of the gases with stopcock grease. Three of these were usually sealed in parallel on each chlorine and sulfur dioxide storage trap so three runs could be made without the necessity of changing the trap.

It was necessary to keep the temperature constant  $\pm 0.2^{\circ}$  C. as the accuracy of the pressure measurements depended upon the temperature control. A De Kotinsky regulator was used to control the temperature and a heating unit of nichrome wire was the source of heat. The reaction chamber, stirring pump and gage were enclosed in an asbestos box with the heating unit at

the bottom (3, Fig. 1). The windows were of thin pyrex plate. A thermometer (11, Fig. 1) in contact with the circulating gas was enclosed in a glass tube which was sealed directly into the reaction chamber.

## B. Preparation of the Materials

### 1. Chlorine

The chlorine was prepared by heating dry cupric chloride (14) in a vacuum. The brown powder was dried at  $110^{\circ}$  C. for at least four hours to insure against any moisture being present. The storage trap for the chlorine is shown in Fig. 2. This storage trap was sealed to a system of traps in series so that the chlorine could be fractionated at least six times, saving only the middle fraction in each process, before it was sealed into the storage trap. The dry cupric chloride, about 150 grams in an Erlenmeyer flask, was sealed to the other end of the system of traps. The system was then evacuated with a hy-vac pump which was sealed off after the first gases had been driven off by gently heating the cupric chloride.

After the system was sealed off the traps next to the cupric chloride were cooled in a freezing mixture of chloroform and solid carbon dioxide. Upon heating the brown powder, a slow stream of chlorine gas was liquefied in the second trap. After about thirty cubic centimeters of the liquid had formed, the source was sealed off and a series of fractionations left five

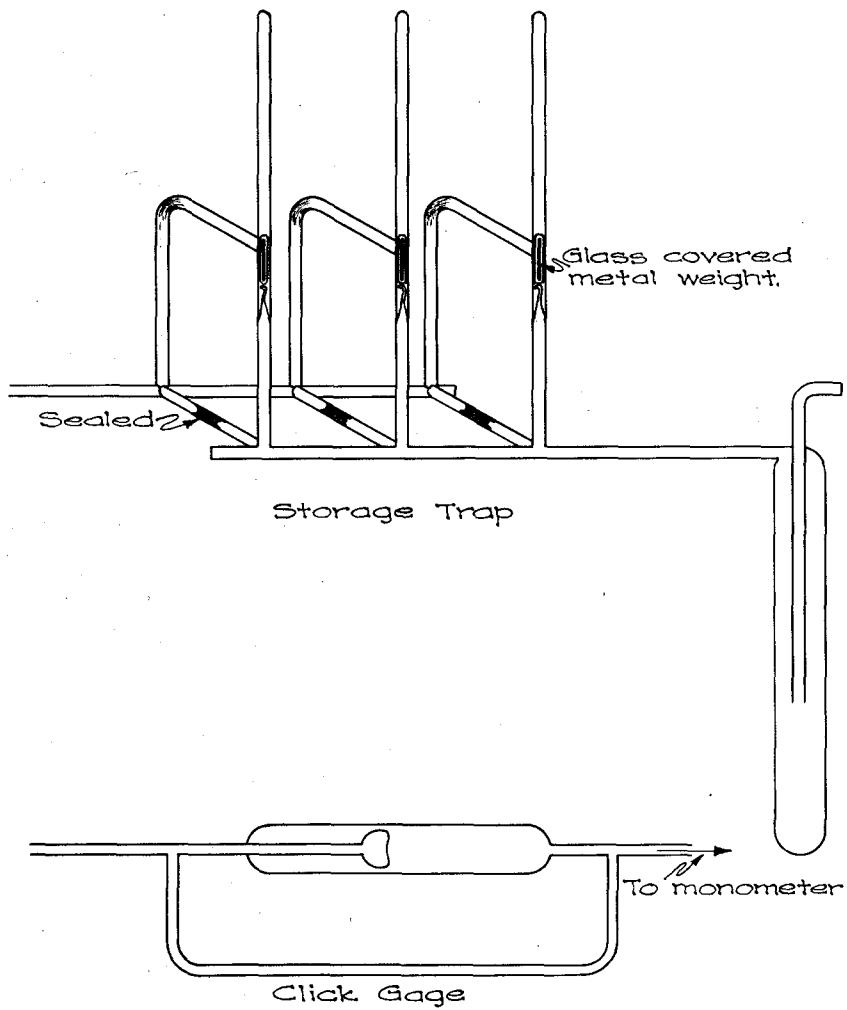
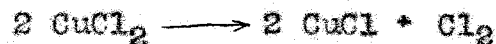


Fig. 2. Storage trap and click gage.

cubic centimeters of the pure liquid which was sealed in the storage trap. The trap was kept in a freezing mixture until the chlorine was used up as the pressure of the liquid chlorine at room temperature was about eight atmospheres, and this was too high a pressure to be safe in ordinary pyrex glassware. The purity of the gas was checked by bubbling some slowly through mercury in which it completely dissolved. This proved to be the most efficient way of preparing dry chlorine free from any trace of oxygen or nitrogen. There was no contact with the air after the system was pumped down, and the powder was heated long enough to drive out any small amount of residual moisture which might have been present.

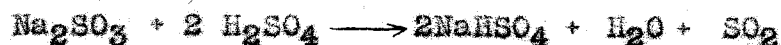
In the first runs, which were made as trial runs, ordinary tank chlorine was used. A long induction period was found at the start of the reaction, sometimes thirty or forty hours, and this could probably be due to some impurities which were present in the tank chlorine. The reaction in the above preparation is given as:



at a temperature of about 450° C. to insure a slow steady stream of chlorine gas.

## 2. Sulfur dioxide

The sulfur dioxide was prepared by the action of sulfuric acid on sodium sulfite.





The gas was passed through water which was saturated with the gas to remove any water-soluble gases which might be present. It was passed through a sulfuric acid solution to remove any sulfur trioxide, fractionated slowly through a tube of calcium chloride to dry the gas, and sealed into a system similar to that used for the fractionation of the chlorine.

This system was evacuated after the sulfur dioxide was frozen solid with liquid air. It was fractionated six times after the vacuum apparatus was sealed off, frozen out into the storage trap similar to the one used for chlorine, and sealed on the line at 8, Fig. 1. This liquid was also kept in a freezing mixture to prevent the possibility of the pressure being too great for the pyrex glass.

### 3. Sulfuryl chloride

There have been many catalysts used in the preparation of this liquid; their use is described by Schwarz and Kunzer (15). Activated charcoal heated in an atmosphere of chlorine was used in the preparation of the sulfuryl chloride for the experiments to check the decomposition of this liquid at a temperature near 100° C. It was found that a mixture of sulfur dioxide and chlorine, cooled to about -40° C. in the presence of the activated charcoal, was converted to sulfuryl chloride nearly one hundred per cent within a few seconds. At room temperature the conversion is slower and not complete. The liquid was separated from the catalyst by distillation under reduced pres-

sure and the volatile gases were pumped off. It was stored in pyrex traps, sealed off with thin glass tips which could be broken after sealing the trap to the reaction bulb in which the decomposition was to take place.

### C. Measurements

#### 1. The reaction

The total elapsed time of the reaction was usually of the order of ninety to one hundred fifty hours, depending upon the pressures of the gases present and the amount of light absorbed during the process. The water jacket around the mercury arc, the lens, the window into the constant temperature box and the window of the reaction chamber were all pyrex glass and very little light of a wave length less than 4000 A could enter the reaction chamber. Chlorine was the only gas of the mixture of sulfur dioxide, chlorine and sulfuryl chloride which absorbed radiation in this region of the spectrum and, as chlorine was the only absorber, the amount of energy absorbed by the mixture was directly proportional to the pressure of the chlorine present.

The temperature of the reaction was 70° C. The total pressure of the reactants was never greater than atmospheric pressure, and under these conditions the sulfuryl chloride which was formed remained in the gaseous state. Sulfuryl chloride boils at 70° C. at one atmospheric pressure.

The usual procedure which was followed in carrying out a reaction began with the evacuation of the system after the storage traps of sulfur dioxide and chlorine had been sealed to the line (8, and 15, Fig. 1). Stopcocks at ( $C_1$  and  $C_3$ ) were closed during the process.  $C_1$  connected the apparatus to the atmosphere and  $C_3$  was the stopcock between the click gage and the manometer. It was necessary to have a by-pass around the click gage (12, Fig. 1) so that the evacuation would not take place against the thin glass diaphragm. This protected the gage and by careful manipulation the one diaphragm was used throughout this set of experiments.

The evacuation always took over ten hours, and sometimes two days, and was carried out with the reaction chamber heated to  $100^{\circ}$  C. This heating was necessary to remove the last traces of gases adhering to the walls of the reaction chamber. The progress of the evacuation was followed on the McLeod gage (18, Fig. 1). This gage was built with three stages, and pressures could be read from one millimeter down to a flat vacuum. The system was always evacuated to a pressure of less than  $10^{-5}$  mm. Hg.

After the evacuation was completed the by-pass around the click gage was sealed off at  $S_8$  and  $S_9$ , Fig. 1. Stopcock ( $C_3$ ) was then opened after the manometer had been pumped down to about two centimeters pressure. With  $C_3$  open an increase in pressure inside the reaction chamber could be followed with the manometer operating against the click gage. The vacuum

pumps and McLeod gage were sealed off from the main reaction system at  $S_3$ ,  $S_5$  and  $S_6$ , Fig. 1. This prevented the gases which were to be admitted later from coming in contact with mercury or stopcock grease.

The next step was the admission of the gases. Extreme caution had to be followed to protect the diaphragm of the click gage. Chlorine was admitted first. It was stored in the trap shown in Fig. 2., which had been sealed on the line at  $L_5$ , Fig. 1, before the evacuation was started. One of the glass tips between the storage trap and the line was broken, and the gas was admitted to the reaction chamber very slowly by regulating the temperature of the liquid chlorine by the addition of a small amount of chloroform or solid carbon dioxide to the Dewar flask which was used to cool the liquid. The increase in pressure of the gas in the chamber was followed by the click gage. A three-way stopcock ( $C_4$ , Fig. 1) was used to allow air to enter above the manometer with  $C_3$  closed. This aided the regulation of the pressure above the manometer and finer adjustments were made by the leveling bulb ( $L_7$ , Fig. 1). An excess of chlorine gas was admitted and the line sealed off at  $S_7$ . The remaining chlorine in the trap was cooled again and the small tube sealed off near the broken tip. The gas was then ready to be used in a later experiment.

The pressure of the chlorine in the reaction chamber was checked at room temperature by the mercury manometer and the click gage; the gas was heated to  $70^{\circ}$  C., at which temperature

the reaction was to be performed, and the pressure was determined at the higher temperature. The gas was cooled back down to room temperature and the exact amount to be used in the experiment was liquefied in trap 4 and sealed off at  $S_1$ . The amount of chlorine which was liquefied was determined from the difference in pressure of the original gas and that which was left after liquefaction. This trap was equipped with a by-pass around the seal that could be opened back to the reaction chamber by breaking a small glass tip. The excess chlorine which was not liquefied and sealed off in trap 4 was pumped from the reaction chamber by breaking the glass tip at 10 which connected the reaction chamber to the evacuation apparatus. As soon as the system was evacuated the line was sealed off at  $S_4$  and the sulfur dioxide was admitted to the reaction chamber after a glass tip was broken at 9.

The same procedure was used in controlling the rate at which the sulfur dioxide was admitted into the reaction chamber as was used with the chlorine. The line was closed by sealing the tube at  $S_2$  as soon as the correct amount of sulfur dioxide had been admitted. The small tube through which the sulfur dioxide entered was sealed after the storage trap was again cooled. The pressure was checked with the click gage at room temperature, and the gas was heated to  $70^\circ$  and the pressure was again checked. In the meantime, the chlorine was kept cool in trap 4 with the freezing mixture of solid carbon dioxide and chloroform.

The chamber was cooled to room temperature and the chlorine gas again admitted to the reaction chamber by breaking the small glass tip at 4. The total pressure always checked the sum of the pressures of the individual gases within the limit of the experimental error of  $\pm 0.3$  mm.

In order to prove whether or not there was any dark reaction between the two gases, they were allowed to stand mixed in the reaction chamber at  $70^{\circ}$  without any light for about one hundred hours in two of the preliminary experiments. There was no appreciable change in pressure which confirmed the findings of Le Blanc, Andrich and Kangro (7) that the dark reaction between the two gases was not appreciable in the absence of a catalyst.

In later experiments no light was admitted into the reaction chamber for five hours after the gases were mixed. This gave a chance to check to make certain there was no dark reaction. The pump (2, Fig. 1) was run at intervals before the light was turned on to avoid the possibility of a dead space between the valves. After the mercury arc was turned on the pump was running continuously except when pressure readings were taken. These readings were taken about every hour in the first part of the reaction and at two to five-hour intervals as the reaction proceeded. The pump could not be run while these readings were being taken because of the change in pressure of the system due to the sudden surge of the piston back and forth.

The following outline is given for the pressure readings

and the order in which they were taken for Experiment No. 15. Approximately equal pressures of the chlorine and sulfur dioxide were desired in this specific experiment and the total pressure of the two when heated to  $70^{\circ}$  must be between 48 and 56 cm. Hg so that the  $\alpha$ -bromonaphthalene manometer could be used to measure the pressure difference as the reaction proceeded. The mercury manometer was used in the process of measuring the pressures of the gases as they were admitted because the range of the  $\alpha$ -bromonaphthalene manometer was limited to a difference in pressure of about ten centimeters of mercury.

After the system was evacuated and the vacuum apparatus sealed off from the reaction chamber, the reading on the mercury manometer which caused the gage to click showed a difference in the heights of the mercury columns in the manometer of 49.55 cm. Hg. There was a vacuum on the side of the click gage which was connected to the reaction system. The pressure necessary to click the gage was measured as the difference between the atmospheric pressure, as read on the barometer, and the pressure shown by the manometer. The barometric pressure was 74.09 cm. Hg, giving a difference of 24.44 cm. of Hg which was necessary to click the gage. The pressure inside the reaction chamber increased as the chlorine gas was admitted. The pressure measured on the manometer system was always 24.44 cm. Hg greater than the true pressure inside the reaction chamber because this was the pressure necessary to cause the diaphragm to click.

Chlorine gas was admitted until the pressure reached 44.69 cm. Hg at 25°. The gas was then frozen out into the trap 4 until the pressure in the reaction chamber reached 21.70 cm. Hg. This chlorine was sealed off (22.99 cm.) and the residual chlorine gas pumped from the reaction chamber. The sulfur dioxide was then admitted and sealed into the chamber at 22.77 cm. Hg pressure.

The glass tip was broken in trap 4, and the chlorine gas mixed with the sulfur dioxide. The pump 2 was started to insure complete mixing. The total pressure of the two gases was 45.76 cm. Hg at 25°. The reaction chamber was heated to 70° and the total pressure of the mixture at this temperature was 52.43 cm. Hg. Adding 24.44 cm. Hg to 52.43 the sum of the two gave a value which did not vary appreciably from the barometric pressure and the  $\alpha$ -bromonaphthalene manometer was used to measure the pressure change after the reaction was started.

## 2. Light intensity

There was no device available for the measurement of the absolute intensity of the light so a linear thermopile was constructed. It was calibrated against a standard lamp obtained from the Electrical Testing Laboratories of New York.\*

The method used in the construction of the thermopile

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\* (Electrical Testing Laboratories, 80th Street and East End Avenue, New York City.)



was similar to that described by Coblenz (16). Modifications were necessary in order to use the materials which were available. The receivers were thin sheets of tin obtained from an old condenser. These sheets were thoroughly washed in alcohol and cut in blocks 2 mm. by 4 mm. The wires for the thermal junctions were extruded bismuth (.004 inch in diameter) and silver (.0015 inch in diameter). They were obtained from Baker and Company, Inc.\*

The thermocouple units (Fig. 3) were assembled individually and then mounted on the bakelite case to form the completed thermopile (Fig. 4). The silver and bismuth wires which formed the hot junction were joined together and fastened to the center receiver with a small globule of pure tin. The ends of the silver wire were first tinned by touching a small drop of molten metal. These wires were handled by smooth ivory-tipped tweezers. The silver wire was fastened to the tin receiver by touching the tinned end to the receiver and heating until the tin was melted. This was heated gently with a small soldering iron which was made from a piece of nichrome wire that was filed smooth on the end and which had a resistance in series to control the temperature. The heat capacity of the unit was kept as low as possible, and any excess tin was rubbed off with the hot iron. The bismuth wires were much harder to handle because of their softness. Extreme care was necessary in handling them at any time. They were moved with a soft piece

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\* (Baker and Company, Inc., 54 Austin Street, Newark, New Jersey.)

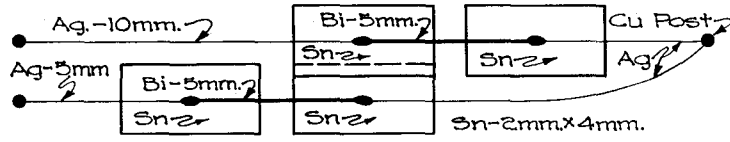


Fig. 3. Thermocouple Unit.

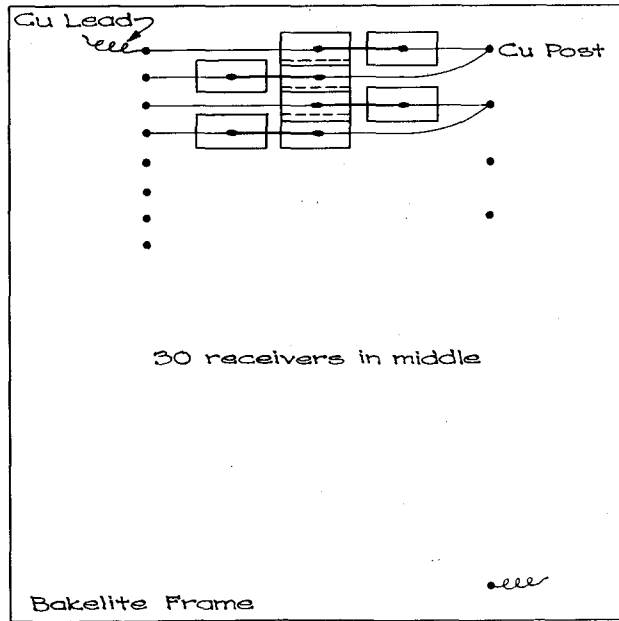


Fig. 4. Thermopile.

of wood which had been cut very thin on the end so that it would be pliable enough not to injure the soft wires. The bismuth wire was placed end to end with the silver wire which had been joined to the tin receiver; the silver wire was slowly heated by touching it near the junction with the hot iron, and it readily alloyed with the bismuth, forming a smooth junction. This was the center receiver or hot junction.

The cold junction was made in a similar manner, but a shorter piece of silver wire was used. The silver wire was first joined to a tin receiver which was the same size as the center receiver; this was then joined to the end of the bismuth wire from the center receiver by gently heating the silver wire. These units were tested with a milliammeter by a very small current from a dry cell and a high resistance. This method made it possible to find those junctions which had a high resistance due to a poor contact between the two metals. This was learned the hard way because the first thermopile had to be dismantled and three of the junctions repaired.

The junction of silver and bismuth formed the back of the receivers. They were mounted with the smooth face towards the light and 2 cm. back of a slit which was cut 3 mm. wide in a piece of bakelite. In the process of mounting the units the bakelite frame was fastened securely on a desk top with a flat piece of wood extending through the slit so that the center receivers could rest on this flat surface while they were being soldered to the copper posts. These posts were made

of short pieces of copper wire which were forced into small holes drilled in the bakelite. The individual units were placed in position, resting on the flat wooden surface, and the silver wires were soldered to the copper posts. The units were mounted in series and overlapped about three quarters of a millimeter so that there would be no space between them. They were insulated from each other by touching the back of the lower receivers with a thin alcoholic solution of shellac which held them securely in position when it dried. There were thirty receivers with an over-all length of about 5.0 cm.

The front of the receivers was blackened with a thin suspension of lamp black in alcohol and shellac. This took four or five coats as it had to be applied in thin layers so as to give a smooth surface which appeared black to the eye.

A slit (2.5 mm. in width) was cut in a thin sheet of copper and mounted outside the bakelite surface. This was protected from air currents by a thin sheet of pyrex glass. The assembled thermopile was mounted in a wooden case which could be attached to a support at the end of the reaction chamber. An auxiliary slit and micrometer screw were used with a linear thermopile to give a fine adjustment for a change in position.

The thermopile was calibrated against the standard lamp by the method described by Coblentz (17). A White potentiometer was used to measure the potential developed by the thermopile in order to minimize the effects of the stray currents and thermal changes which are present in the ordinary galvanometer-

thermopile arrangement. The voltages read on the potentiometer with the radiation from the standard lamp falling on a slit area of 101.25 mm.<sup>2</sup> were .00280 volts with the lamp at one foot from the thermopile, .00150 volts at two feet, .00080 volts at three feet and .00030 volts at four feet. The null point was read on a galvanometer with a sensitivity of 1160 mm. per A. This galvanometer had a resistance of 52,000 ohms in series and 33,000 ohms in parallel.

Although the thermopile was calibrated against the white light of the standard lamp and used to measure the blue-violet light (4358 A) of the mercury arc, the error made in assuming that the receivers were nonselective in their response to light of different wave lengths was of the order of a fraction of one per cent (18).

The thermopile was placed in position with the slit vertical and in the center of the beam of light which had passed through the reaction chamber filled with chlorine. It gave a reading of .00021 volts. The same slit was used on a large surface photocell<sup>\*</sup> in the same position as the thermopile had been, and this gave a reading of .00341 volts on the White potentiometer. These values were checked three times on each measuring device. The full beam of 4358 A light after passing through the reaction chamber filled with chlorine was then allowed to fall on the photocell, and this gave a reading of .01790 volts. The full beam without the chlorine in the tube had given a reading of .27566 volts.

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\*Bradley Company, Inc., 82 Meadow Street, New Haven, Conn.

The calculations for the quantum efficiency from these data will be given in the interpretation of results.

#### IV. INTERPRETATION OF RESULTS

##### A. Light Absorption and Quantum Efficiency

###### 1. Absorption of light by the chlorine

Photochemical reactions are characterized by the fact that the absorption of light is necessary for the reaction to take place. In this reaction of sulfur dioxide and chlorine, in which the absorption in the visible region of the spectrum is due solely to the chlorine, the primary process is one that depends upon the change in the chlorine molecule soon after absorption. The initial effect is an electronically excited chlorine molecule which has become activated by the absorption of a quantum of radiation. This can be shown as:



with  $\text{Cl}_2^*$  indicating an electronically excited state.

After the molecule has become activated by the absorption of light, it is possible for it to lose this energy or part of it in any of the following ways:

1. Fluorescence
2. Deactivation by collisions or by contact with a third body
3. Dissociation
4. Reactions with other molecules

Fluorescence may be defined as the emission of radiation

by a chemical system following the absorption of radiant energy. If a molecule has become activated by the absorption of radiation and has no collisions during its lifetime in the excited state, it must re-emit this energy or part of it by fluorescence, or it must dissociate. Kistiakowski (19) has made a thorough study of the fluorescence of chlorine molecules upon illumination with visible light. He found that considerably less than five per cent of the absorbed light energy is re-emitted by chlorine as fluorescence. He used chlorine which was sufficiently pure to exclude any possibility of a photochemical reaction. Unless this precaution was taken some of the energy might be used up in a chemical reaction, but no appreciable difference was found in the light absorption between moist and dry chlorine.

The electronically excited chlorine could be deactivated by collisions with other molecules present or by transferring this energy to the walls of the surrounding vessel. Since diatomic and polyatomic molecules possess a large number of quantum levels the loss of excitation energy by this method could occur in small steps, and it could be gradually dissipated in small steps and transformed into heat energy.

Kistiakowski (19) has indicated that chlorine molecules which have been activated by light in the region of continuous absorption probably dissociate into atoms. The convergence limit begins at 4785 Å, and light of this wave length possesses enough energy to dissociate the molecule into two normal atoms;



this energy of dissociation is given as 2.48 electron volts (20). Dissociation probably causes the formation of one normal atom ( $2P_{3/2}$ ) and an excited or metastable ( $2P_{1/2}$ ) atom with a difference in energy between the two states of about 0.1 electron volt (21). A difference in behavior of these two types of atoms may exist, but a categorical statement as to this difference cannot be justified by the evidence which is available (22). Rollefson and Eyring (23) have given theoretical justifications for a triatomic chlorine molecule ( $Cl_3$ ). There is no definite way of establishing a real difference between reaction mechanisms in which a  $Cl_3$  molecule is postulated and one in which there is a triple collision between a chlorine atom, a chlorine molecule and a third body. Becker and Rollefson (24) state that many reactions may be explained satisfactorily by the use of the triatomic molecule of chlorine. It has been shown though by Sherman and Sun (25) that reactions involving such molecules, if they were present, would be very slow and that little advantage could be gained by the use of  $Cl_3$ .

The fourth way in which activated chlorine may lose the energy of excitation is by a reaction with other molecules present. It has been necessary to postulate the dissociation of the activated molecule into atoms in order to explain the high quantum yield of the various chain reactions in which chlorine is the absorbing molecule. If the activated molecule reacts directly as a unit with other molecules present, the primary quantum yield should be the same as the initial absorption as long as energy is not lost in any other way except

in this reaction. Thus, if the excited molecule reacts directly with another molecule to form a stable product, the over-all quantum yield should be unity. The accumulation of experimental evidence from various sources indicates that very few photochemical processes involve the direct reaction of electronically excited molecules, but rather that in most cases the primary process leads to the dissociation of the absorbing molecule.

## 2. The quantum efficiency

The quantum efficiency for the reaction:



was calculated by using a linear thermopile to measure the intensity of the light which had been absorbed by the chlorine. The method for the measurement of the light intensity has been given. The light from the mercury arc was passed through a Corning filter (No. 7) to render it nearly monochromatic. The light which passed through the filter was nearly pure 4358 Å but the intensity was decreased considerably (less than 14% of the original light of this wave length passed through). The curve in Fig. 5 shows the change in pressure of the reacting system with time for Experiment 16. In the starting mixture there was a chlorine pressure of 24.96 cm. Hg and the pressure of the sulfur dioxide was 27.26 cm. Hg. The temperature of the system was 70° C. It was from the data of this reaction that the quantum efficiency was calculated. The experimental data are given in Table 1.

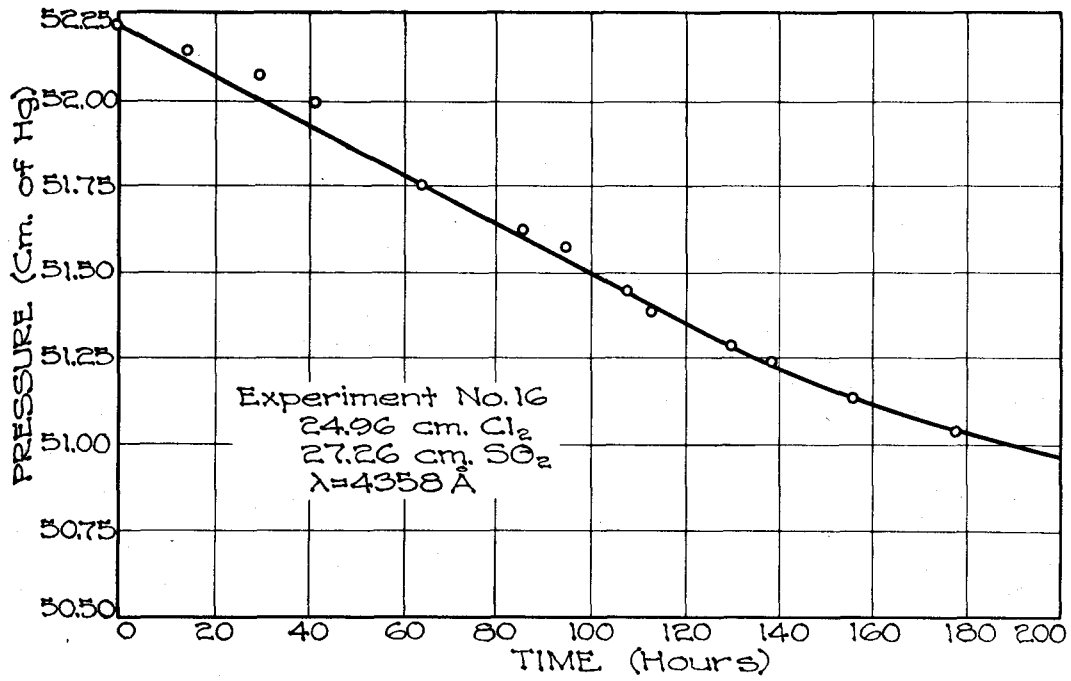


Fig. 5. Experiment 16

Table 1  
Data for Fig. 5, Experiment 16

Time (hrs.)	Pressure (total) cm. Hg
0	52.22
15	52.15
30	52.08
41.5	52.00
64.5	51.75
86.0	51.63
95.0	51.58
108.0	51.45
113.0	51.39
130.0	51.29
139.0	51.24
156.0	51.13
178.0	51.04
202.0	50.96

The average change in pressure over a ten-hour period has been taken as .73 mm. Hg (corrected to 0° C.):

Volume of reaction system	=	3595 ml.
ergs/sec passing through reaction chamber before Cl <sub>2</sub> gas was admitted	=	8819
ergs/sec after Cl <sub>2</sub> gas was admitted to chamber	=	572
ergs/sec absorbed by Cl <sub>2</sub>	=	8819 - 572
		= 8247

Assuming a perfect gas:

$$PV = nRT$$

$$\frac{PV}{RT} = n \quad \text{where } n = \text{number of moles}$$

$$\frac{\frac{24.96}{76.0} \times 3.595}{.08206(273.1 + 70)} = .0419 \text{ moles of chlorine gas present}$$

$$.0419 \times 6.02 \cdot 10^{23} = 2.524 \cdot 10^{22} \text{ molecules of chlorine.}$$

Molecules of gas reacting in 10 hours as shown by a pressure change of .73 mm. Hg:

$$\frac{\frac{0.73}{76.0} \times 3.595}{.08206(273.1 + 70)} = 1.26 \cdot 10^{-4} \text{ moles}$$

$$1.26 \times 10^{-4} \times 6.02 \times 10^{23} = 7.584 \times 10^{19} \text{ molecules reacting/10 hours.}$$

Number of quanta absorbed:

$$h = h \frac{c}{\lambda} \quad \text{energy of incident light}$$

$$h = \text{Plancks constant} = 6.624 \times 10^{-27} \text{ erg sec.}$$

$$c = \text{velocity of light}$$

$$\lambda = \text{wave length of incident light.}$$

$$\frac{(6.624 \times 10^{-27})(3.00 \times 10^{10})}{4.358 \times 10^{-5}} = 4.560 \times 10^{-12} \text{ ergs/sec. energy in light quantum}$$

$$\frac{\text{total energy absorbed}}{\text{energy/quantum}} = \text{number of quanta absorbed}$$

$$\frac{8.247 \times 10^3}{4.560 \times 10^{-12}} = 1.808 \times 10^{15} \text{ quanta absorbed/sec.}$$

$$(1.808 \times 10^{15})(10 \times 60 \times 60) = 6.511 \times 10^{19} \text{ quanta absorbed/10 hours}$$

Quantum efficiency:

$$\text{Quantum efficiency} = \frac{\text{No. of molecules reacting}}{\text{No. of quanta absorbed}}$$

$$\frac{7.584 \times 10^{19}}{6.511 \times 10^{19}} = 1.2 \pm 0.2$$

This value for the quantum efficiency is based on an average value for the intensity of the light which was absorbed in the process of the reaction. Since there was an appreciable variation in the voltage on the A.C. line on which the mercury arc was operated, there was a corresponding variation in the intensity of the incident beam from the arc. It was hoped that there would be a constant voltage A.C. generator available for the operation of the arc and thus insure a constant value for

the intensity, but war priorities prevented the delivery of this generator. The extent of this variation in intensity of the arc can be seen from the readings taken for the intensity of full light of the mercury arc after passing through the reaction chamber, which contained chlorine at a pressure of 26.34 cm. Hg and sulfur dioxide at a pressure of 26.09 cm. Hg. These readings were taken of the current from the photocell over a twenty-four hour period and were read upon a milliammeter with a scale which could be read to approximately one milliampere. They are given in Table 2.

Table 2  
Variation of Light Intensity over Twenty-four Hour Period

Time	Milliamperes
7:00 A.M.	470
8:00 A.M.	462
9:00 A.M.	454
10:00 A.M.	438
11:00 A.M.	431
12:00 A.M.	439
1:00 P.M.	424
4:00 P.M.	435
7:00 P.M.	453
9:00 P.M.	469
11:00 P.M.	465
2:00 A.M.	469
3:00 A.M.	470

This shows a variation of 46 milliamperes or approximately 10 per cent of the maximum.

The other assumptions which have been made in the determination of the quantum efficiency, such as the non-selectivity of the receivers on the thermopile, the linearity of readings on the potentiometer and that the molecules act as a perfect gas, are very small as compared with the fluctuations of the light source.

An indication as to the value of the quantum efficiency for this reaction was given by Benhoeffter (10) as approximately one thousandth that of phosgene. The value which he gave for phosgene was  $2.76 \times 10^3$ , and a value which was of the order of one thousandth of that would be comparable to the value of 1.2 given above. He also stated that the reaction of sulfur dioxide and chlorine appeared to follow the equivalence law, and the value of 1.2 found in this investigation would further substantiate this statement. Although not too great an accuracy can be claimed for this value of the quantum efficiency because of the variation in light intensity, it clearly indicates that this reaction tends to follow the equivalence law and has a quantum efficiency of approximately one.

In many photochemical reactions of this type in which chlorine is the absorber, such as:



it is necessary to postulate the dissociation of the activated



chlorine molecule into atoms in order to explain the high quantum yields of approximately  $10^6$  for the formation of HCl and approximately  $10^3$  for the formation of  $\text{COCl}_2$  (10). In this reaction of sulfur dioxide and chlorine it would not be necessary to postulate the dissociation of the chlorine into atoms in order to carry on the chain because the quantum efficiency of approximately one would indicate that the reaction could possibly take place between the activated chlorine molecule and a molecule of sulfur dioxide. This would be possible as the mean life of the excited halogen molecule is about  $10^{-8}$  sec., and under the conditions of this experiment the time between collisions would be of the order of  $10^{-10}$  sec. (27).

#### B. The Reaction

It has been established by LeBlanc, Andrich and Kangro (7) and by Bonhoeffer (10) that this reaction of sulfur dioxide and chlorine can be followed by the pressure change of the system as long as the light which is absorbed does not fall in the range which could be absorbed by either the sulfur dioxide or the sulfuryl chloride after it has formed. To prove certain of this fact, the boiling point and the density of the product formed in the reaction were checked.

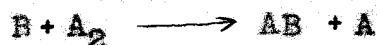
A brief survey will be given of some of the developments which have led to the modern concepts on photochemical kinetics of gaseous systems. Bodenstein (28) in 1913, when calculating

the quantum yields of a few reactions which had been studied quantitatively, came to the conclusions that the observable rate in a photochemical reaction was the combined effect of a sequence of reactions and the first one, the primary process, is strictly determined by the equivalence law. The reactions which follow depend upon the chemical constitution of the photochemical system. The importance of his work is given by the definite acceptance of the equivalence law and an explanation for the deviations from this law.

Nernst (29) advanced the concept of the primary photochemical process as a dissociation of the molecules on the absorption of a quantum of energy. The reactions of the free atoms produced were thought to be the cause of the deviations from the equivalence law. He stated that in a reaction of the type:



if the subsequent reaction:



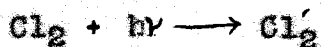
is thermodynamically possible, the atoms A would be continually regenerated and a large number of reacting molecules would result for each quantum of light which was absorbed.

Stern and Volmer (30) suggested that the light absorption does not cause dissociation but excitation of the molecules. The excited molecules possess a high reaction ability and can undergo a chemical reaction on collision with a non-excited molecule present in the reacting system. The excited molecules

could lose energy by re-emission of radiation or by inelastic collisions, accounting for the quantum yields in several cases which were below that of the equivalence law. They criticized the theory of Nernst on the primary dissociation of molecules, basing their criticism upon the observations of the spectrum of iodine vapor which shows that the iodine molecules remain undissociated even upon absorption of radiation energy greater than the heat of dissociation.

Franck (31) has correlated the theories on excitation and dissociation by pointing out that the immediate result of light absorption is the formation of an excited molecule, but the excited molecule can undergo dissociation even without a collision. The absorption of light by a molecule increases the energy of the electronic system with a change in the oscillatory energy of the atoms. If the increase in the oscillatory energy is great enough, the binding forces between the atoms may be weakened to such an extent that the molecule would dissociate.

From theoretical considerations it seems to be possible for the photochemical reaction of sulfur dioxide and chlorine to proceed after the absorption of light by the chlorine:



either as an activated molecule reacting with  $\text{SO}_2$ :



or through decomposition of the activated molecule into a normal and an excited atom of chlorine, and these atoms in

turn reacting by a three-body collision with the sulfur dioxide to form the sulfuryl chloride:



An intermediate compound could possibly be formed:



and this could react with another atom of chlorine:



A series of plots are given in Figs. 6 to 9 inclusive, which show the change in pressure of the over-all reactions with time. Pressures of the absorbing molecule have been varied from 1.78 cm. Hg in Fig. 6 to 40.52 cm. Hg in Fig. 9. The reactions were carried out at 70° C. with the full light of the mercury arc and the pressure change in Experiments 9, 10, 11, 12, and 13 were followed by the mercury manometer and the pressure change was followed by the  $\alpha$ -bromonaphthalene manometer in Experiments 14 and 15. The data for each graph are given in tabular form in a table following each of the graphs. These data were taken from a large plot of a smooth curve from the experimental points.

Experiment 12, which is shown in Fig. 6, was carried out from an original pressure of 34.01 cm. Hg. Of this total pressure, 1.78 cm. was chlorine and 32.23 cm. was SO<sub>2</sub>. The reaction was nearly complete in one hundred hours although it had not reached a completely stationary state. The reaction was continued to a total of one hundred and thirty hours at which

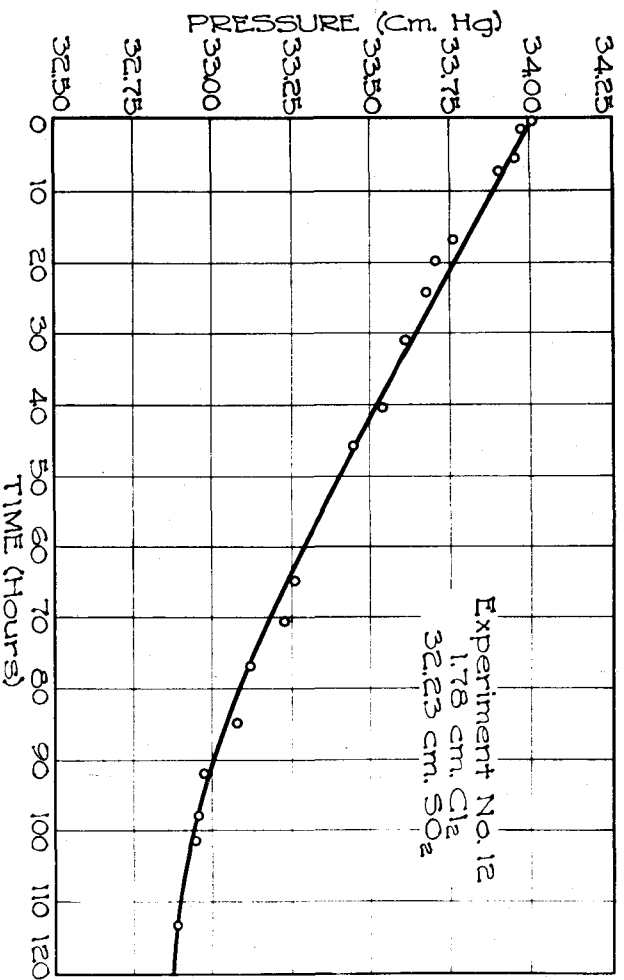


Fig. 6. Experiment 12

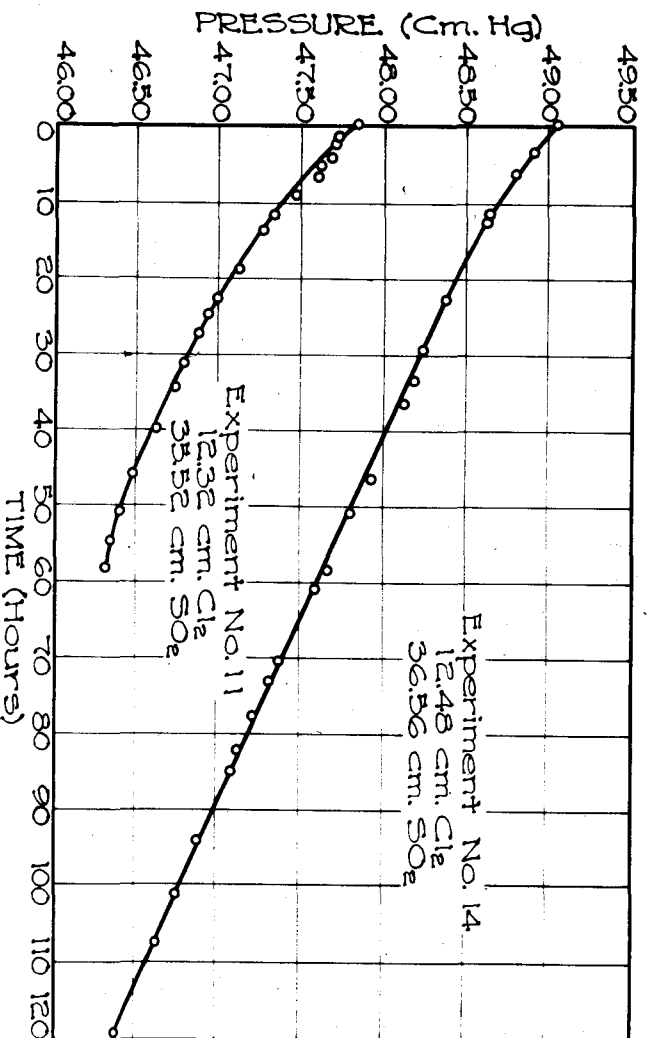


Fig. 7. Experiments 11 and 14

Table 3  
Data for Experiment 12

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	34.01	0.00	1.78	0.2504	32.23	1.5083	0.561	0.0552
5	33.92	0.09	1.69	0.2279	32.14	1.5070	0.591	0.0526
10	33.85	0.07	1.62	0.2095	32.07	1.5061	0.617	0.0505
15	33.78	0.07	1.55	0.1903	32.00	1.5052	0.645	0.0484
20	33.72	0.06	1.49	0.1732	31.94	1.5045	0.671	0.0467
25	33.66	0.06	1.43	0.1553	31.88	1.5035	0.699	0.0442
30	33.61	0.05	1.38	0.1399	31.83	1.5028	0.725	0.0434
35	33.56	0.05	1.33	0.1239	31.78	1.5022	0.752	0.0419
40	33.51	0.05	1.28	0.1072	31.73	1.5015	0.731	0.0403
45	33.47	0.04	1.24	0.0934	31.69	1.5009	0.807	0.0391
50	33.43	0.04	1.20	0.0792	31.65	1.5002	0.833	0.0379
55	33.40	0.03	1.17	0.0682	31.62	1.5000	0.855	0.0370
60	33.37	0.03	1.14	0.0569	31.59	1.4997	0.874	0.0362

Table 4

Data for Experiment 11

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	47.84	0.00	12.32	1.0906	35.52	1.5505	0.0812	0.3467
5	47.64	0.20	12.12	1.0831	35.32	1.5480	0.0826	0.3428
10	47.45	0.19	11.93	1.0766	35.13	1.5457	0.0838	0.3395
15	47.27	0.18	11.75	1.0700	34.95	1.5435	0.0851	0.3361
20	47.10	0.17	11.58	1.0637	34.78	1.5413	0.0864	0.3330
25	46.95	0.15	11.43	1.0581	34.63	1.5393	0.0873	0.3302
30	46.82	0.13	11.30	1.0531	34.50	1.5378	0.0885	0.3276
35	46.70	0.12	11.18	1.0484	34.38	1.5363	0.0895	0.3252
40	46.59	0.11	11.07	1.0442	34.27	1.5349	0.0903	0.3231
45	46.49	0.10	10.97	1.0406	34.17	1.5336	0.0911	0.3214
50	46.41	0.08	10.89	1.0370	34.09	1.5326	0.0919	0.3195
55	46.33	0.08	10.81	1.0338	34.01	1.5316	0.0925	0.3178
60	46.27	0.06	10.75	1.0314	33.95	1.5308	0.0930	0.3167

Table 5

Data for Experiment 14

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	49.04	0.00	12.48	1.0962	36.56	1.5630	0.08013	0.3413
5	48.84	0.20	12.28	1.0892	36.36	1.5606	0.08144	0.3378
10	48.63	0.16	12.12	1.0835	36.20	1.5587	0.08251	0.3348
15	48.55	0.13	11.99	1.0788	36.07	1.5572	0.08341	0.3324
20	48.42	0.13	11.86	1.0741	35.94	1.5556	0.08432	0.3300
25	48.31	0.12	11.74	1.0697	35.82	1.5541	0.08511	0.3278
30	48.20	0.11	11.63	1.0656	35.71	1.5528	0.08598	0.3257
35	48.10	0.10	11.53	1.0618	35.61	1.5516	0.08672	0.3238
40	48.00	0.10	11.43	1.0581	35.51	1.5504	0.08747	0.3219
45	47.90	0.10	11.33	1.0542	35.41	1.5491	0.08827	0.3200
50	47.80	0.10	11.23	1.0504	35.31	1.5479	0.08904	0.3181
55	47.70	0.10	11.13	1.0465	35.21	1.5467	0.08985	0.3161
60	47.60	0.10	11.03	1.0426	35.11	1.5454	0.09066	0.3142

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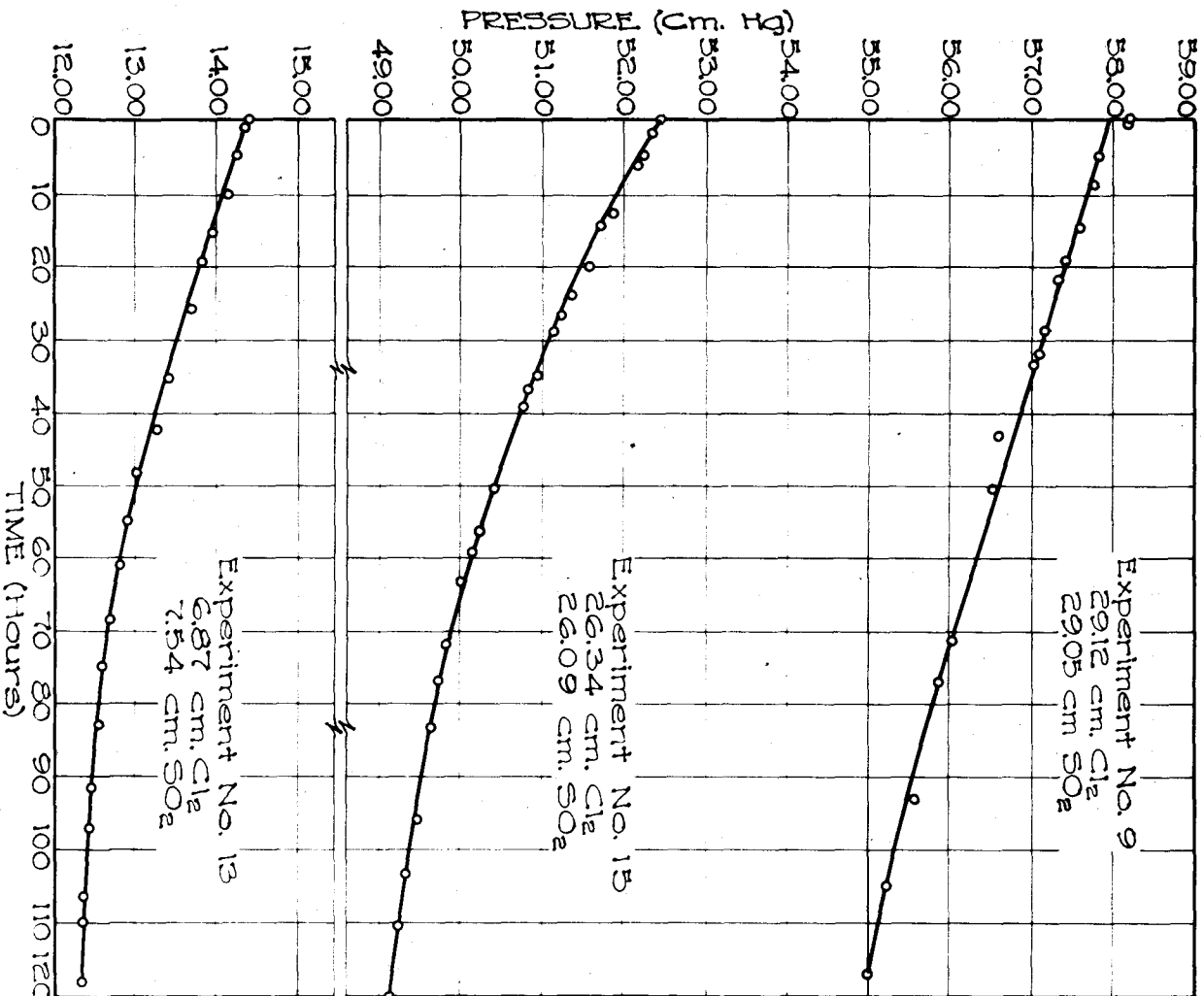


FIG. 8. Experiments 9, 13 and 15

Table 6  
Data for Experiment 13

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	14.41	0.00	6.87	0.8370	7.54	0.8774	0.1456	0.9122
5	14.25	0.16	6.71	0.8267	7.38	0.8681	0.1491	Constant
10	14.10	0.15	6.56	0.8169	7.23	0.8591	0.1524	
15	13.95	0.15	6.41	0.8060	7.08	0.8500	0.1560	
20	13.81	0.15	6.26	0.7966	6.93	0.8407	0.1597	
25	13.66	0.14	6.12	0.7868	6.79	0.8319	0.1634	
30	13.52	0.14	5.98	0.7767	6.65	0.8228	0.1672	
35	13.37	0.14	5.84	0.7664	6.51	0.8136	0.1712	
40	13.24	0.14	5.70	0.7559	6.37	0.8041	0.1754	
45	13.11	0.13	5.57	0.7459	6.24	0.7882	0.1795	
50	12.98	0.13	5.44	0.7356	6.11	0.7860	0.1838	
55	12.86	0.12	5.32	0.7259	5.99	0.7774	0.1882	
60	12.74	0.12	5.20	0.7160	5.87	0.7686	0.1927	

Table 7

Data for Experiment 15

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	52.43	0.00	26.34	1.4206	26.09	1.4165	0.03797	1.025
5	52.19	0.24	26.10	1.4166	25.85	1.4126	0.03832	Constant
10	51.96	0.23	25.87	1.4128	25.62	1.4086	0.03866	
15	51.72	0.23	25.64	1.4072	25.39	1.4047	0.03916	
20	51.50	0.22	25.42	1.4052	25.17	1.4009	0.03934	
25	51.28	0.22	25.20	1.4014	24.95	1.3971	0.03968	
30	51.07	0.21	24.99	1.3978	24.74	1.3934	0.04001	
35	50.88	0.20	24.79	1.3943	24.54	1.3899	0.04034	
40	50.70	0.18	24.61	1.3925	24.36	1.3867	0.04050	
45	50.52	0.18	24.43	1.3879	24.18	1.3835	0.04094	
50	50.35	0.17	24.26	1.3849	24.01	1.3804	0.04122	
55	50.19	0.16	24.10	1.3820	23.85	1.3775	0.04150	
60	50.03	0.16	23.84	1.3791	23.69	1.3746	0.04177	

Table 8  
Data for Experiment 9

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	58.17	0.00	29.12	1.4642	29.05	1.4632	0.03433	1.003
5	57.87	0.29	28.83	1.4598	28.76	1.4588	0.03469	Constant
10	57.70	0.19	28.64	1.4570	28.57	1.4559	0.03493	
15	57.53	0.17	28.47	1.4540	28.40	1.4533	0.03516	
20	57.38	0.15	28.32	1.4521	28.25	1.4510	0.03531	
25	57.22	0.16	28.16	1.4496	28.09	1.4486	0.03552	
30	57.09	0.13	28.03	1.4476	27.96	1.4465	0.03568	
35	56.95	0.14	27.89	1.4455	27.82	1.4444	0.03585	
40	56.82	0.13	27.76	1.4434	27.69	1.4423	0.03603	
45	56.70	0.12	27.64	1.4415	27.57	1.4404	0.03618	
50	56.57	0.13	27.51	1.4395	27.44	1.4384	0.03635	
55	56.44	0.13	27.38	1.4374	27.31	1.4363	0.03653	
60	56.33	0.11	27.27	1.4357	27.20	1.4346	0.03667	

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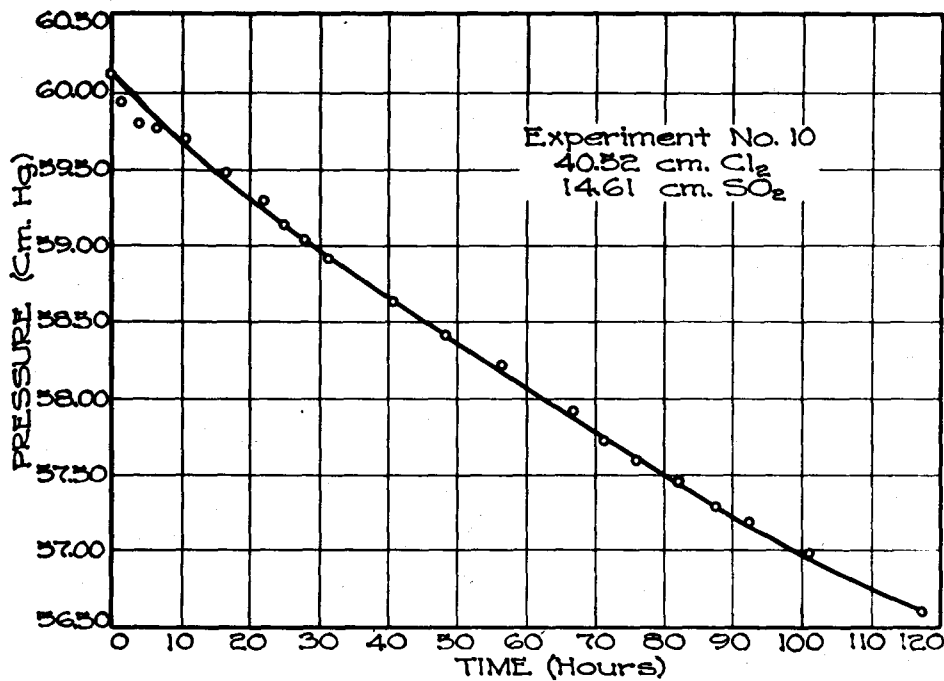


Fig. 9. Experiment 10

Table 9

## Data for Experiment 10

Time hrs.	Pressure cm. Hg	$\Delta P$ cm. Hg	Pressure Cl <sub>2</sub>	Log Pressure Cl <sub>2</sub>	Pressure SO <sub>2</sub>	Log Pressure SO <sub>2</sub>	$\frac{1}{P_{Cl_2}}$	$\frac{P_{Cl_2}}{P_{SO_2}}$
0	60.13	0.00	40.52	1.6077	19.61	1.2925	0.0247	2.006
5	59.90	0.23	40.29	1.6052	19.38	1.2874	0.0248	2.074
10	59.69	0.21	40.06	1.6029	19.17	1.2826	0.0249	2.091
15	59.50	0.19	39.89	1.6009	18.98	1.2783	0.0250	2.102
20	59.33	0.17	39.72	1.5990	18.81	1.2744	0.0251	2.112
25	59.17	0.16	39.56	1.5973	18.65	1.2707	0.0253	2.121
30	59.03	0.14	39.42	1.5957	18.51	1.2674	0.0254	2.130
35	58.90	0.13	39.29	1.5943	18.38	1.2644	0.0255	2.138
40	58.78	0.12	39.17	1.5929	18.26	1.2615	0.0255	2.145
45	58.67	0.11	39.06	1.5917	18.15	1.2589	0.0256	2.152
50	58.57	0.10	38.96	1.5906	18.05	1.2565	0.0257	2.158
55	58.47	0.10	38.86	1.5895	17.95	1.2541	0.0257	2.165
60	58.38	0.09	38.77	1.5886	17.86	1.2518	0.0258	2.171

time no change in pressure could be detected on the mercury manometer over a ten-hour period. The total change in the pressure over this period of one hundred and thirty hours was 1.14 cm. The ratio of the SO<sub>2</sub> to Cl<sub>2</sub> in the original mixture was over sixteen to one. About 63.2 per cent of the original chlorine reacted to form sulfuryl chloride. Assuming a stationary state for the reaction at one hundred and thirty hours, the equilibrium constant would be:



$$K_p = \frac{P_{\text{SO}_2\text{Cl}_2}}{P_{\text{SO}_2} P_{\text{Cl}_2}}$$

$$K_p = \frac{1.14}{(1.78 - 1.14)(32.23 - 1.14)} = 5.9 \times 10^{-2}$$

Figure 7 shows Experiments 11 and 14. The total pressure in No. 11 was 47.84 cm. Hg of which 12.32 cm. was due to chlorine and 35.53 cm. was due to SO<sub>2</sub>. In No. 14 the total pressure was 49.04 cm. Hg, which was made up of 12.48 cm. Cl<sub>2</sub> and 36.56 cm. SO<sub>2</sub>. The pressure of the SO<sub>2</sub> was about the same in these experiments as it was in the previous Experiment No. 12, while the pressure of the Cl<sub>2</sub> was about seven times as great. Experiment No. 11 was stopped at sixty hours because the lead-in tube had not been sealed off inside the constant temperature box, and there was a possibility of some of the sulfuryl chloride condensing in the tube outside the box. The change in the pressure of the system at the end of sixty hours was 1.48 cm.

Experiment No. 14 was continued for a total of one hundred and sixty-eight hours, and at this time there was still a very small change in pressure over a ten-hour period. The pressure change in this experiment was measured on the auxiliary manometer which contained  $\alpha$ -bromonaphthalene. The total pressure change was 3.45 cm. Hg, which gave a  $K_p$  of  $9.4 \times 10^{-2}$ . The percentage of the original  $Cl_2$  used up was 27.5.

Figure 8 shows Experiments 9, 13 and 15. These were carried out with approximately equal pressures of  $Cl_2$  and  $SO_2$ . In No. 13 the total pressure was 14.43 cm. Hg of which 6.87 cm. was due to  $Cl_2$  and 7.54 cm. was due to  $SO_2$ . The reaction was complete in one hundred and thirty-five hours with a pressure change of 2.35 cm. The percentage of the  $Cl_2$  used up was 34.4.  $K_p = 9.9 \times 10^{-2}$ . In Experiment No. 15 the starting pressure of the mixture of the two gases was 52.43 cm. Hg. Of this pressure, 26.34 cm. was due to  $Cl_2$  and 26.09 was due to  $SO_2$ . The time of the experiment was one hundred and sixty hours, and there was still a slight change in pressure which amounted to about .4 mm. in ten hours. The total pressure change was 3.91 cm. and 14.9 per cent of the  $Cl_2$  was used up.  $K_p = .78 \times 10^{-2}$ . Experiment No. 9 had a starting pressure of 58.17 cm. Hg of which 29.12 cm. was due to  $Cl_2$  and 29.05 cm. was due to  $SO_2$ . The time of the run was one hundred and fifty hours, and the total pressure change was 4.07 cm. There was 14.0 per cent of the original chlorine used up, and  $K_p$  was equal to  $.66 \times 10^{-2}$ .



Figure 9, which was Experiment No. 10, had an initial pressure of 60.13 cm. Hg of which 40.52 cm. was due to  $\text{Cl}_2$  and 19.61 cm. was due to  $\text{SO}_2$ . The reaction was complete in one hundred and twenty hours. The total pressure change was 3.57 cm. and 8.8 per cent of the  $\text{Cl}_2$  was used up in the reaction.  $K_p = .66 \times 10^{-2}$ . Table 10 gives the data from these graphs in tabular form.

Table 10  
Data from Graphs

Experiment No.	Total Pressure (cm. Hg)	$P_{\text{Cl}_2}$ (cm. Hg)	Time Completed Reaction (hrs.)	Total Change of Pressure (cm. Hg)	% $\text{Cl}_2$ Reacting	$K_p$
12	34.01	1.78	130	1.14	63.2	$5.9 \times 10^{-2}$
13	14.43	6.87	135	2.35	34.4	$9.9 \times 10^{-2}$
11	47.84	12.32	60 (not complete)	1.48	12.2	(not complete)
14	49.04	12.43	168	3.45	27.5	$9.4 \times 10^{-2}$
15	52.43	26.34	160	3.91	14.9	$0.78 \times 10^{-2}$
9	58.17	29.12	150	4.07	14.0	$0.66 \times 10^{-2}$
10	60.13	40.52	120	3.57	8.8	$0.66 \times 10^{-2}$

It was thought that further insight into the mechanism and order of the reaction might be gained if various rate laws were assumed and the data plotted graphically. The change in the pressure with time of the constituents of the reaction is known, and an idea as to the approximate order of the reaction with respect to the various reactants may be obtained by

plotting  $P^{1-n}$  against time (where  $P$  is the pressure of one of the reactants and  $n$  is the order of the reaction). A straight line would be obtained when  $n$  is the order of the reaction, except where  $n$  is equal to one; then a straight line would be obtained by plotting  $\log P$  against time. The data for these plots are given in Tables 3 to 9, inclusive, and were obtained from large plots of pressure against time from the experimental values.

It should be recalled that these reactions have been carried out with heterochromatic light which is absorbed only by the  $Cl_2$ . The reaction was stirred continuously to prevent any filter effect and varying concentrations throughout the system. There was very little variation in the absorption of light by the  $Cl_2$  throughout the length of the reaction chamber.

Figure 10 shows a plot of the  $\log P_{Cl_2}$  against time for the various reactions. Straight lines were obtained in this plot for all the reactions except Experiment 10 and the latter part of Experiment 11. In Experiment 10 the original pressure of the  $Cl_2$  was purposely made much larger than the pressure of the  $SO_2$  in order to study the effect of an excess of  $Cl_2$ . In Experiment 11 a short length of an entrance tube was not sealed off inside the constant temperature box, and there is the probability that after the reaction had proceeded a short time some of the  $SO_2Cl_2$  may have condensed in that tube which was at room temperature. The straight lines indicate that the

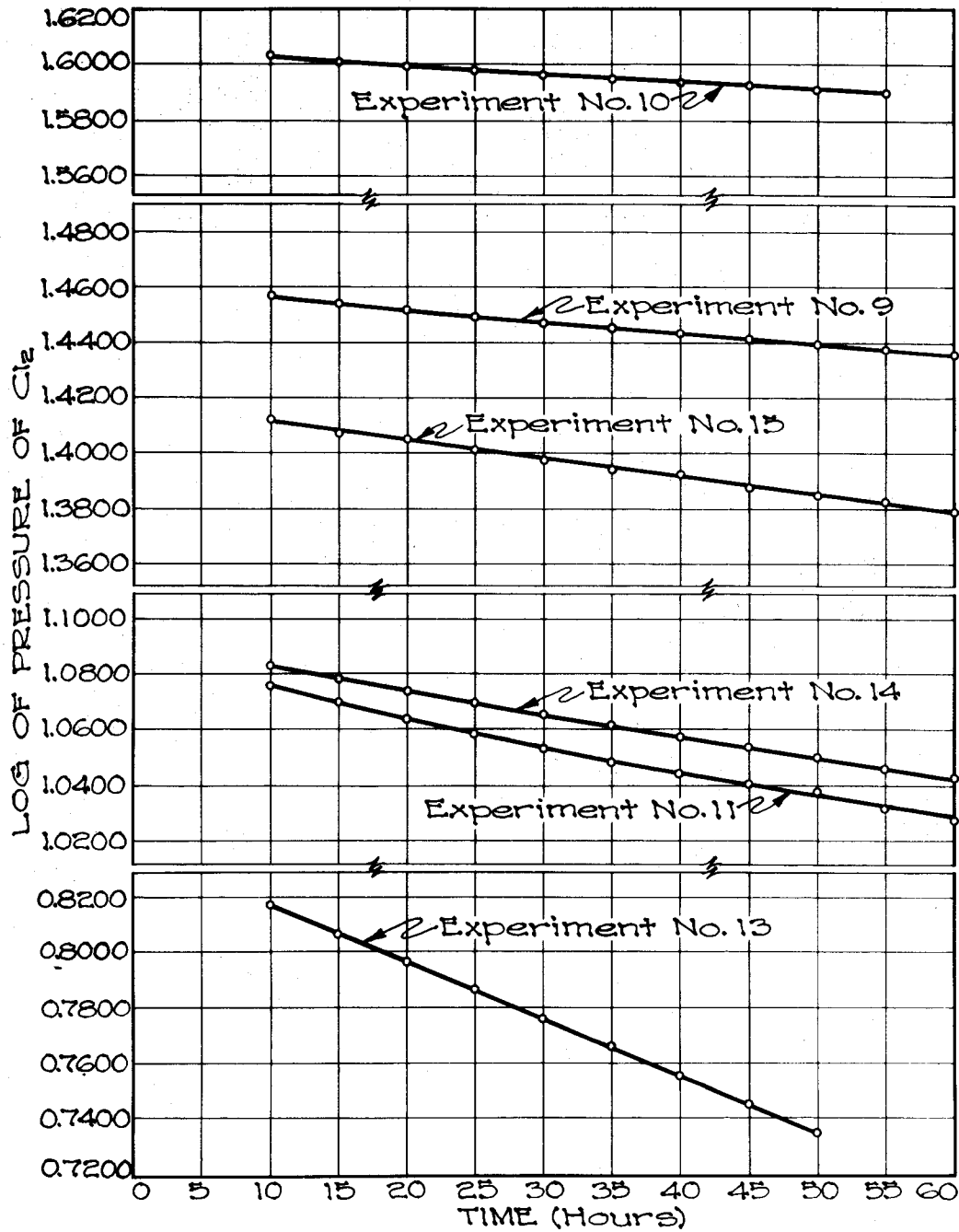


Fig. 10. Change in Log P<sub>Cl<sub>2</sub></sub> with Time

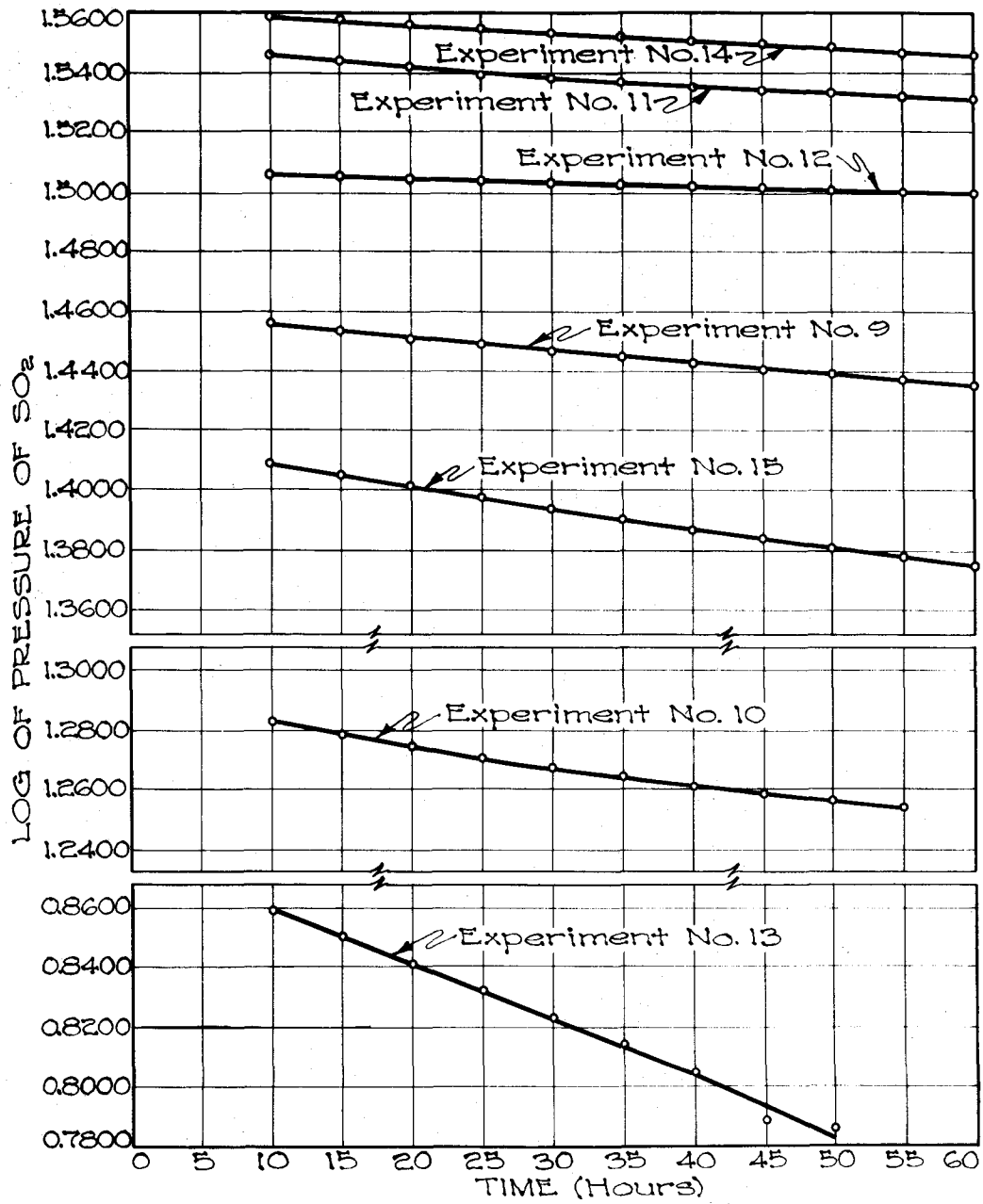


Fig. 11. Change in Log P<sub>SO<sub>2</sub></sub> with Time

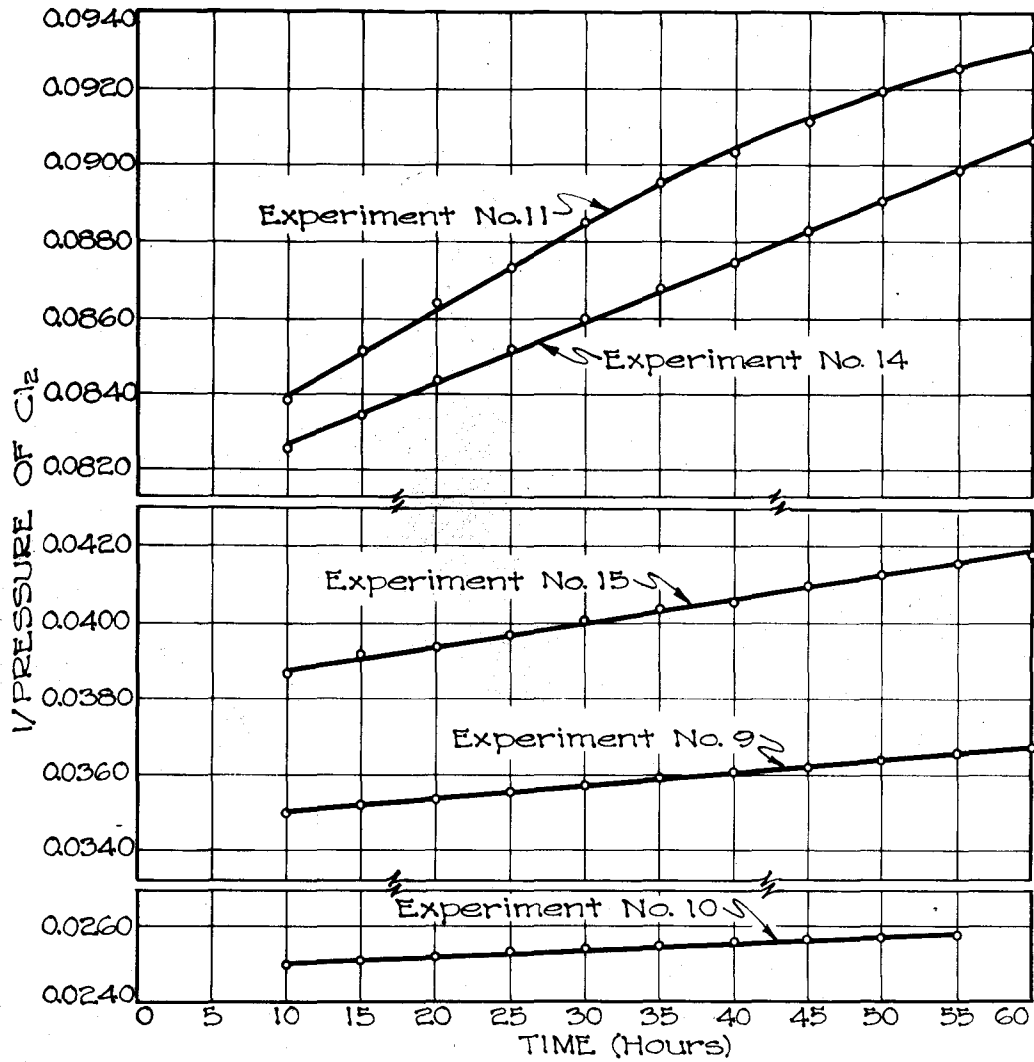


Fig. 12. Change in  $\frac{1}{P_{C12}}$  with Time

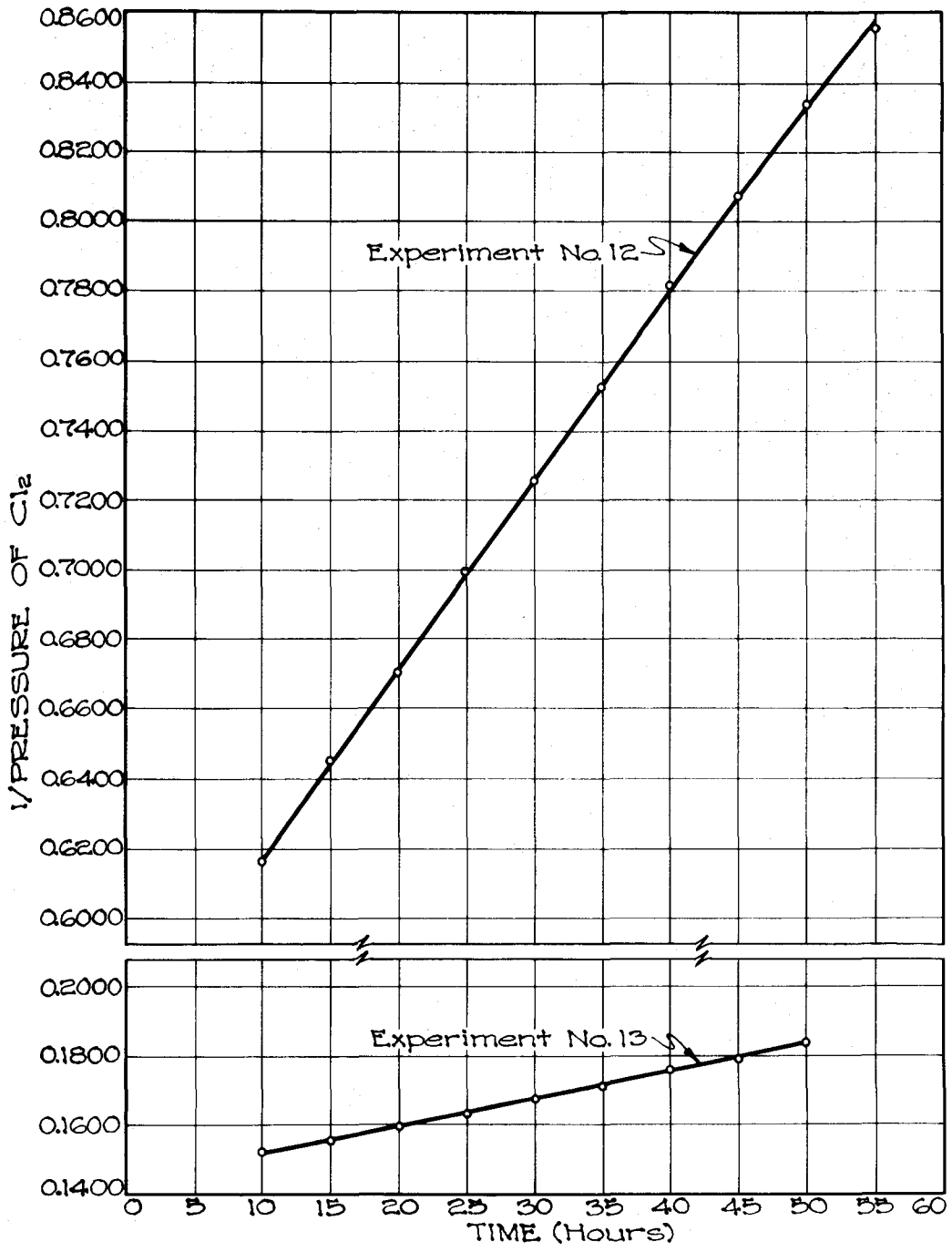


Fig. 12 (Cont.). Change in  $\frac{1}{P_{Cl_2}}$  with Time

rate of formation of  $\text{SO}_2\text{Cl}_2$  within these pressure ranges follows the equation:

$$\frac{d(\text{SO}_2\text{Cl}_2)}{dt} = k(\text{Cl}_2)$$

The steeper slopes at lower pressures show that the reaction proceeds faster at lower pressures of  $\text{Cl}_2$ .

In Fig. 11 the  $\log P_{\text{SO}_2}$  is plotted against time. These lines are curved, except those in which the pressure of the  $\text{SO}_2$  was nearly equal to that of the  $\text{Cl}_2$ . These lines show that the formation of sulfuryl chloride is not a first-order reaction with respect to the  $\text{SO}_2$  within these pressure ranges.

In Fig. 12 the value of the reciprocal of the pressure of the chlorine is plotted against time. This plot gives curved lines for these reactions in which the chlorine pressure and the sulfur dioxide pressure were nearly equal, indicating that the reaction is not of the second order.

### C. Dissociation of Sulfuryl Chloride

The dissociation of  $\text{SO}_2\text{Cl}_2$  was first studied by Trautz (32) who gave values for the equilibrium constant at temperatures ranging from 100 to 200° C. Arai (33) measured the equilibrium at temperatures of 30, 40 and 50° C. and gave expressions for  $\log K_p$ , for  $\Delta F$  and for  $\Delta H$  as a function of temperature. The data given by these two investigators showed a marked difference, and it seemed wise to experimentally determine the

dissociation constants for this decomposition in the temperature range of 70 to 125° C.

A flask of 160 cc. capacity was used in these determinations and animal charcoal which had been carefully washed with ether, dried, and heated to 900° C. was used as the catalyst to speed up the decomposition. The flask was evacuated and an excess of pure  $\text{SO}_2\text{Cl}_2$  added and then heated to the desired temperature with a very small opening to the atmosphere so the excess gas could escape. The time of heating for constant values varied from six hours at 70° C. to three hours at 125° C.

After heating, the tip was sealed off and the flask weighed with the  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2$  and  $\text{Cl}_2$  mixture. It was then evacuated and weighed again to determine the weight of the  $\text{SO}_2\text{Cl}_2$ ,  $\text{SO}_2$  and  $\text{Cl}_2$  mixture. The flask was then filled with water and the volume determined.

The apparent molecular weight of the mixture was determined, assuming the gas laws to hold, and the degree of dissociation was calculated from:

$$PV = \frac{g}{M_2} RT$$

$$\alpha = \frac{M_1 - M_2}{M_2(\nu - 1)}$$

$M_2$  = apparent molecular weight

$M_1$  = molecular weight of sulfuryl chloride

$\nu$  = number of molecules formed in dissociation

$\alpha$  = degree of dissociation

The equilibrium constant,  $K_p$  in atmospheres, was calculated



from the experimental values for the dissociation of sulfuryl chloride by the equation:

$$K_p = \frac{\alpha^2}{1 - \alpha^2} P \quad P = \text{pressure in atmospheres}$$

The experimental values for the dissociation and the calculated values of  $K_p$  are given in Table 11.

Table 11  
Dissociation and Equilibrium Constant

Temperature, °C.	Pressure, mm.*	% Dissociated	$K_p$ (Atmosphere)
67.0	741.4	59.84	0.564
85.0	742.5	77.75	1.494
100.0	722.3	87.47	3.098

\*Corrected to 0° C.

The equilibrium constant increases with temperature as the  $\Delta H$  is positive and heat is absorbed in the process of dissociation. An increase in pressure decreases the degree of dissociation at any temperature although the equilibrium constant remains the same. This would be expected because there is an increase in the number of molecules as the reaction proceeds, and an added pressure would tend to force the reaction back towards the lower pressure.

The heat of the reaction ( $\Delta H$ ) can be determined from the values of  $K_p$  at two temperatures from the integrated equation:

$$\log \frac{K_{p2}}{K_{p1}} = \frac{\Delta H}{2.303R} \frac{T_2 - T_1}{T_2 T_1} \quad T = ^\circ K$$

This gives a value for  $\Delta H$  of 12,910 calories with the substitution of the values of  $K_p$  given above at the temperature of 85 and 100° C.

The hypothetical heat of reaction at absolute zero ( $\Delta H_0$ ) is now determined, assuming the heat capacity relations will hold down to absolute zero:

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p dT$$

The value of  $\Delta C_p = C_p$  (products) -  $C_p$  (reactants)

$$\Delta C_p = (C_{pCl_2} + C_{pSO_2}) - C_{pSO_2Cl_2}$$

The value for  $\Delta C_p$  for the dissociation of sulfuryl chloride has been given by Aril (33) as:

$$\Delta C_p = -1.1 + .008T - 1.86 \times 10^{-6} T^2$$

The substitution of this value into the equation:

$$\Delta H = \Delta H_0 + \int_0^T \Delta C_p dT$$

and integrating:

$$\Delta H = \Delta H_0 - 1.1T + 4 \times 10^{-3} T^2 - .62 \times 10^{-6} T^3$$

This gives a value of  $\Delta H_0$  as:

$$\Delta H_0 = 12,795 \text{ cal.}$$

using the  $\Delta H$  given above at  $100^\circ \text{C}$ . and assuming  $\Delta H$  constant over the  $15^\circ$  temperature range between 85 and  $100^\circ \text{C}$ .

The integration constant (I) can now be calculated using the  $\Delta H_0$  of the reaction and the free energy change ( $\Delta F$ ) as calculated from:

$$\Delta F = -2.303 RT \log K_p$$

$$R = 1.987$$

$$K_p = 3.098 \text{ at } 100^\circ \text{C.} \\ \text{(experimental value)}$$

$$\Delta F = -2.303 \times 1.987 \times 373.1 \log 3.098 \\ = -838 \text{ cal.}$$

$$\Delta F = \Delta H_0 + 1.1 \times 2.303 T \log T - 2.0 \times 10^{-3} T^2 + .21 \times 10^{-6} T^3 \\ + IT$$

Substituting the values for  $\Delta F$  at  $100^\circ \text{C}$ . and  $\Delta H_0$ :

$$- 838 = 12,795 + 1.1 \times 2.303 \times 373.1 \log 373.1 - 2 \times 10^{-3} \\ \times 373.1^2 + .21 \times 10^{-6} \times 373.1^3 + IT$$

$$I = -42.18$$

The average value of I found from the  $\Delta F$  at the three experimental temperatures was:

$$I = -42.26$$

The general equation for the calculation of the free energy at any temperature for the dissociation of sulfuryl chloride is given:

$$\Delta F = 12,795 + 2.53 T \log T - 2.0 \times 10^{-3} T^2 + .21 \times 10^{-6} T^3 \\ - 42.26T$$

This equation was used to calculate the value for  $\Delta F$  at  $40^\circ \text{C}$ ., at which temperature Arii has given an experimental value for  $K_p$ . This calculated value of  $\Delta F$  was found to be:

$$\Delta F = 1,340 \text{ cal. at } 40^{\circ} \text{ C.}$$

This gives a calculated value of  $K_p$  at this temperature:

$$K_p = 0.10 \text{ atm. at } 40^{\circ} \text{ C.}$$

The mean experimental value given by Arii was:

$$K_p = 0.051 \text{ atm. at } 40^{\circ} \text{ C.}$$

Following the same procedure the value of  $K_p$  was obtained at  $110.5^{\circ} \text{ C.}$  Trautz has given an experimental value:

$$K_p = 3.7 \text{ at } 110.5^{\circ} \text{ C. with a possible error of } \pm 0.5$$

The value of  $K_p$  calculated from the above equation determined from this investigation was:

$$K_p = 4.7 \text{ at } 110.5^{\circ} \text{ C.}$$

These calculated constants show fair agreement with the experimental values of the other investigators in the temperature ranges in which their data were determined. The data given by Arii were used to calculate the value of  $K_p$  at  $110.5^{\circ} \text{ C.}$  (his data were obtained between  $30$  and  $50^{\circ} \text{ C.}$ ):

$$K_p = 1.03 \text{ at } 110.5^{\circ} \text{ C.}$$

The equation reported by Trautz gave the following values of  $K_p$ :

$$K_p = 28.6 \text{ at } 110.5^{\circ} \text{ C.}$$

$$K_p = 0.64 \text{ at } 110.5^{\circ} \text{ C.}$$

#### D. Calculation of the Free Energy

Enough data have been found available in the literature to calculate the free energy of the molecule ( $\text{SO}_2\text{Cl}_2$ ) by statistical methods. These data are necessary:

1. Vibrational frequencies of the molecule from Raman spectra (34)(35).
2. Electron diffraction values which show the molecular model, the positions of the atoms, and the interatomic distances (36).

The steps in the calculation of the free energy are:

1. Assignment of the vibrational frequencies to the various modes of vibration.
2. Evaluate the translational and rotational contributions of the molecule to the entropy by the equation:

$$S_{t,r}^{\circ} = \frac{3}{2} R \ln M + 4R \ln T - R \ln s + \frac{1}{2} R \ln ABC + 265.289$$

M = molecular weight

s = symmetry number

ABC = product of the principal moments of inertia of the molecule.

3. Evaluate the contribution of the vibrations to the entropy of the molecule.
4. The value of the free energy is obtained from the sum of the contribution of the translation, rotation and vibration to the free energy.

The electron diffraction patterns show that the molecule is a distorted tetrahedron with the sulfur in the center. The S-O distances are 1.43 Å and the S-Cl distances are 1.99 Å. The O S O angle is  $119^{\circ} 48'$  and the Cl S Cl angle is  $111^{\circ} 12'$ . The product of the moments of inertia of the molecule has been calculated by Thompson (37) as  $3.88 \times 10^{-113} \text{ gm. cm.}^2$

The diagrams and tables of Kohlrausch (38) have been used in the assignment of the vibrational frequencies to the various modes of vibration which are possible in a molecule of this type. There are five atoms in the molecule and fifteen terms are necessary to describe the energy of the system. This leaves nine normal modes of vibration because three terms are necessary to describe the translation of the molecule and three more are necessary to describe the rotation of the molecule. The symmetry class of the molecule is  $C_{2v}$  with the nine normal modes of vibration falling into four groups. There is a two-fold rotational axis of symmetry  $C_2^z$ . There are two planes of symmetry: the Cl-S-Cl atoms lie in one plane, which is designated as  $x$ , and the O-S-O atoms lie in the other plane, which is designated as  $y$ . The frequencies corresponding to the nine normal modes of vibration are all allowed in the Raman spectrum, and they are assigned to their respective classes in Table 12.

The translational and rotational contribution to the free energy is  $-\left(\frac{F^\circ - E_0^\circ}{T}\right) = S_{t,r}^\circ - 4R$ , and the values for  $SO_2Cl_2$  are substituted in this equation:

$$S_{t,r}^\circ = \frac{3}{2} R \ln M + 4R \ln T - R \ln s - \frac{1}{2} R \ln ABC + 265.289$$

$$M = \text{molecular wt.} = 134.97$$

$$s = 2$$

$$ABC = 3.88 \times 10^{-113}$$

$$S_{t,r}^\circ = 4R \ln T + 21.40$$

$$\begin{aligned} S_{t,r}^\circ - 4R &= 4R \ln T + 21.40 - 4 \times 1.987 \\ &= 4R \ln T + 13.45. \end{aligned}$$

Table 12\*  
Assignment of Raman Frequencies

Class	Frequency ( $\nu$ ) $\text{cm}^{-1}$
A <sup>'</sup> <sub>1</sub>	1190
A <sup>'</sup> <sub>2</sub>	560
A <sup>'</sup> <sub>3</sub>	408
A <sup>'</sup> <sub>4</sub>	214
A <sup>''</sup> <sub>1</sub>	280
B <sup>'</sup> <sub>1</sub>	1415
B <sup>'</sup> <sub>2</sub>	365
B <sup>''</sup> <sub>1</sub>	576
B <sup>''</sup> <sub>2</sub>	380

\*Nomenclature by Kohlrausch, Z. Phys. Chem.,  
B2B, 342. 1935.

This is the translational and rotational contribution to the free energy.

The contributions of the fundamental vibrational frequencies ( $\text{cm.}^{-1}$ ) to the heat capacity, heat content and free energy of a molecule are given as functions of  $\frac{V}{T}$  by Wilson (39). These values are based upon the assumption that the molecule acts as a harmonic oscillator.

$$H^{\circ} - E_{0}^{\circ} = \int_{0}^{T} \Delta C_{p} dT = (H - E_{0}^{\circ}) + RT$$

$$H^{\circ} - E_{0}^{\circ} = \text{heat content at temperature } T, \text{ above absolute zero}$$

$$H_{0} = E_{0}^{\circ} \text{ at absolute zero for a perfect gas}$$

$$F = H - TS$$

$$\frac{F^{\circ}}{T} = \frac{H^{\circ}}{T} - S^{\circ}$$

$$\frac{F^{\circ} - E_{0}^{\circ}}{T} = \frac{H^{\circ} - E_{0}^{\circ}}{T} - S^{\circ}$$

The translational and rotational contribution to the free energy at  $70^{\circ} \text{C.}$ :

$$\begin{aligned} - \left( \frac{F^{\circ} - E_{0}^{\circ}}{T} \right) &= 4 \times 4.575 \log T + 13.45 \\ &= 46.39 + 13.45 \\ &= 59.84 \text{ k.cal.} \end{aligned}$$

$59.84 + 3.422 = 63.26 \text{ k.cal.}$  the total contribution of translation, rotation and vibration to the free energy.



The value of  $\Delta(F^\circ - E_0^\circ)$  for the reaction  $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$  is calculated:

$$\Delta(F^\circ - E_0^\circ) = (F^\circ - E_0^\circ)_{\text{SO}_2} + (F^\circ - E_0^\circ)_{\text{Cl}_2} - (F^\circ - E_0^\circ)_{\text{SO}_2\text{Cl}_2}$$

These values for  $\text{SO}_2$  and  $\text{Cl}_2$  were taken from Cross (40) and from Giaque and Overstreet (41):

$$- \left( \frac{F^\circ - E_0^\circ}{T} \right)_{\text{SO}_2} \text{ at } 70^\circ \text{ C.} = 52.17$$

$$- \left( \frac{F^\circ - E_0^\circ}{T} \right)_{\text{Cl}_2} \text{ at } 70^\circ \text{ C.} = 46.95$$

$$\begin{aligned} \Delta(F^\circ - E_0^\circ) &= - (52.17 + 46.95) - 63.26 \quad 343.1 \\ &= - 12.31 \text{ k.cal.} \end{aligned}$$

A value of  $\Delta E_0^\circ$  is now necessary in order to calculate  $\Delta F^\circ$ . The  $\Delta E_0^\circ$  may be calculated from:

$$\Delta(H^\circ - E_0^\circ) = .88 \text{ k.cal. at } 291^\circ \text{K (37)}$$

if the value of  $\Delta H^\circ$  is known at this temperature. There is an appreciable disagreement in the values of  $\Delta H^\circ$  given in the literature for the dissociation of sulfuryl chloride. They vary from 15.4 k.cal. given by Eckmann and Rossini (42), which they obtained from the heats of formation, to an approximate value of 11.3 k.cal. given by Trautz (32) and 11.1 k.cal. given by Kelley (43). The equation:

$$\Delta H^\circ = 12,795 - 1.1T + 4.0 \times 10^{-3}T^2 - .62 \times 10^{-6}T^3$$

given in the previous section of this thesis has been used to calculate the value of  $\Delta H^\circ$  291°K.

$$\Delta H^\circ = 12,795 - 1.1 \times 291 + 4.0 \times 10^{-3} \times 291^2 - .62 \times 10^{-6} \times 291^3$$

$$\Delta H^\circ = 12,800 \text{ cal. at } 291^\circ\text{K}$$

$$\Delta(H^\circ - E_0^\circ) = .88 \text{ k.cal. at } 291^\circ\text{K}$$

$$\Delta H = 12.80 \text{ k.cal. at } 291^\circ\text{K}$$

$$\Delta E_0^\circ = 12.80 - .88 = 11.92 \text{ k.cal.}$$

The value of the function  $\Delta(F^\circ - E_0^\circ)$  at  $343^\circ\text{K}$  has been given as  $-12.31 \text{ k.cal.}$  The free energy  $\Delta F^\circ$  is calculated:

$$\Delta(F^\circ - E_0^\circ) = -12.31 \text{ k.cal.}$$

and substituting  $\Delta E_0^\circ = 11.92 \text{ k.cal.}$

$$\begin{aligned} \Delta F^\circ &= -12.31 + 11.92 \\ &= -.39 \text{ k.cal. at } 343^\circ\text{K} \end{aligned}$$

These calculations were also made at  $373^\circ\text{K}$  and gave a value for  $\Delta F^\circ$ :

$$\begin{aligned} \Delta(F^\circ - E_0^\circ) &= -13.42 \\ \Delta E_0^\circ &= 11.92 \\ \Delta F^\circ &= -13.42 + 11.92 \\ &= -1.50 \end{aligned}$$

A comparison is shown in Table 13 of these calculated values of  $\Delta F^\circ$  with the  $\Delta F^\circ$  obtained from the equation developed from the experimental data of this investigation. This equation has been given in the preceding section:

$$\Delta F^\circ = 12,795 + 2.53T \log T - 2.0 \times 10^{-3}T^2 + .21 \times 10^{-6}T^3 - 42.26T$$

The corresponding values of previous investigators are also shown in Table 13.

Table 13

$\Delta F^\circ$  Calculated and Experimental  
for the Dissociation of  $\text{SO}_2\text{Cl}_2$

Temperature $^\circ\text{K}$	$\Delta(F^\circ - E_0^\circ)$	$\Delta E_0^\circ$	Calculated	$\Delta F^\circ$ k.cal.		
				Observed		This
				Trautz	Arii	Experiment
343	-12.31	11.92	-0.39	----	+1.08	+0.27
373	-13.42	11.92	-1.50	-0.60	+0.20	-0.84

This comparison shows that the values of  $\Delta F^\circ$  as calculated by statistical methods agree within 0.66 k.cal. of the experimentally determined values of this investigation. The principal sources of error in this calculation could be in the moments of inertia of the  $\text{SO}_2\text{Cl}_2$  and the anharmonicity of the molecule. These sources of error could account for the variation from the experimental values.

## V. SUMMARY

A complete apparatus was assembled in order to carry out the photochemical reaction of sulfur dioxide and chlorine. This apparatus was designed so that the gases would be in contact with only the walls of the containing vessel throughout the course of the reaction. Small glass tips, which could be broken by the use of an electromagnet, were used in preference to stopcocks so that the gases would not be in contact with stopcock grease. The gases had to be circulated during the reaction in order to obtain consistent results.

The quantum efficiency of the photochemical reaction:



was determined at 70° C. using light with a wave length of 4358 Å from a high-pressure mercury arc. The value for the quantum efficiency was found to be 1.2 ± 0.2.

Rate curves for the reaction at 70° C. have been determined for various starting pressures of the two gases. The reaction was found to be first order with respect to the chlorine, and the equation which best describes the curves was found to be:

$$\frac{d(\text{SO}_2\text{Cl}_2)}{dt} = k(\text{Cl}_2)$$

The degree of dissociation of the molecule ( $\text{SO}_2\text{Cl}_2$ ) in the temperature range between 50 and 100° C. was investigated.

The constants for the dissociation were found from the degree of dissociation and these were used to calculate the  $\Delta H$  for the reaction.

The  $\Delta H$  from the dissociation reaction was used in the calculation of the free energy of sulfuryl chloride. This calculation was made from data available in the literature combined with the  $\Delta H$  determined in the dissociation reaction. The calculated values compared favorably with those found in this investigation.

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